

AGM5823 – Tópicos em Química atmosférica

Ozônio troposférico Compostos orgânicos voláteis (COV)

Profa. Adalgiza Fornaro

São Paulo, outubro 2022

Ozônio na troposfera



De onde vem este ozônio?

❖ Troca estratosfera / troposfera

❖ Produção fotoquímica



Para onde vai este ozônio?

❖ Transporte e remoção na superfície

❖ Destruição química *in-situ*

Níveis de ozônio são expressos tipicamente em parte por bilhão por volume (**ppbv** ou **ppb**), que representam a fração de moléculas de ozônio no total de moléculas de ar. Níveis típicos de ozônio (razões de mistura):

| | |
|---|---|
| background natural (pré-industrial): | 10-20 ppb |
| Regiões remotas no Hemisfério Norte: | 20-40 ppb (variando por estação e latitude) |
| Áreas rurais durante eventos de poluição | 80-100 ppb |
| Pico de O ₃ em áreas urbanas durante eventos de poluição | 120-200 ppb |
| Máximo urbano de O ₃ (Los Angeles, Mexico City) | 490 ppb |
| Camada de ozônio estratosférico | 15000 ppb |
| USEPA padrão para a saúde de ozônio (proposta de revisão): | 125 ppb, 1-hora exposição 85 ppb, 8 horas de exposição |
| CONAMA (Brasil) | 80 ppb, 1 hora de exposição |

Cid.Universitária-USP-Ipen - 12/10/2014

| Hora | NO2 µg/m ³ | | CO ppm | | | O3 µg/m ³ | | | MP2.5 µg/m ³ | | |
|-------|--------------------------|--------------------|---------------|-----------|--------------------|-------------------------|-----------|--------------------|----------------------------|------------|--------------------|
| | Média Horária | Índice / Qualidade | Média horária | Média 8 h | Índice / Qualidade | Média horária | Média 8 h | Índice / Qualidade | Média horária | Média 24 h | Índice / Qualidade |
| 1:00 | 88 | 18 | 1.6 | 1 | 4 | 2 | 51 | 20 | 58 | 46 | 73 |
| 2:00 | 87 | 17 | 1.5 | 1.1 | 5 | 1 | 35 | 14 | 52 | 46 | 73 |
| 3:00 | 83 | 17 | 1.3 | 1.2 | 5 | 2 | 23 | 9 | 50 | 45 | 71 |
| 4:00 | 78 | 15 | 1.2 | 1.3 | 6 | 6 | 15 | 6 | 47 | 44 | 70 |
| 5:00 | 47 | 9 | -- | 1.3 | 6 | 18 | 10 | 4 | 48 | 43 | 68 |
| 6:00 | 26 | 5 | 0.6 | 1.3 | 6 | 23 | 9 | 4 | 38 | 42 | 67 |
| 7:00 | 30 | 6 | 0.6 | 1.2 | 5 | 21 | 9 | 4 | 23 | 40 | 64 |
| 8:00 | 40 | 8 | 0.8 | 1.1 | 5 | 50 | 15 | 6 | 32 | 37 | 59 |
| 9:00 | 44 | 9 | 0.7 | 0.9 | 4 | 105 | 28 | 11 | 53 | 36 | 57 |
| 10:00 | 42 | 8 | 0.7 | 0.8 | 4 | 142 | 46 | 18 | 56 | 36 | 57 |
| 11:00 | 31 | 6 | 0.5 | 0.7 | 3 | 167 | 67 | 27 | 44 | 36 | 57 |
| 12:00 | 12 | 2 | 0.4 | 0.6 | 3 | 175 | 88 | 35 | 27 | 36 | 57 |
| 13:00 | 10 | 2 | 0.4 | 0.6 | 3 | 188 | 109 | 52 | 31 | 36 | 57 |
| 14:00 | 8 | 2 | 0.4 | 0.6 | 3 | 174 | 128 | 77 | 28 | 36 | 57 |
| 15:00 | 9 | 2 | 0.4 | 0.5 | 2 | 189 | 149 | 105 | 26 | 36 | 57 |
| 16:00 | 11 | 2 | 0.4 | 0.5 | 2 | 195 | 167 | 134 | 33 | 37 | 59 |
| 17:00 | 15 | 3 | 0.6 | 0.5 | 2 | 193 | 178 | 156 | 44 | 39 | 62 |
| 18:00 | 20 | 4 | 0.6 | 0.5 | 2 | 184 | 183 | 165 | 46 | 40 | 64 |
| 19:00 | 32 | 6 | 0.7 | 0.5 | 2 | 194 | 186 | 171 | 54 | 41 | 65 |
| 20:00 | 51 | 10 | 0.9 | 0.5 | 2 | 136 | 182 | 163 | 49 | 42 | 67 |
| 21:00 | 55 | 11 | 0.9 | 0.6 | 3 | 83 | 168 | 136 | 36 | 43 | 68 |
| 22:00 | 68 | 14 | 1 | 0.7 | 3 | 44 | 152 | 109 | 30 | 42 | 67 |
| 23:00 | 77 | 15 | 1.1 | 0.8 | 3 | 27 | 132 | 83 | 44 | 42 | 67 |
| 24:00 | 96 | 19 | | | | 4 | | 51 | 43 | | 65 |
| | | | 1.3 | 0.9 | 4 | | 108 | | | 41 | |

Cid.Universitária-USP-Ipen - 13/10/2014

| Hora | NO2 µg/m ³ | | CO ppm | | | O3 µg/m ³ | | | MP2.5 µg/m ³ | | |
|----------|--------------------------|-----------------------|------------------|--------------|-----------------------|-------------------------|--------------|-----------------------|----------------------------|---------------|-----------------------|
| | Média Horária | Índice / Qualidade | Média horária | Média 8 h | Índice / Qualidade | Média horária | Média 8 h | Índice / Qualidade | Média horária | Média 24 h | Índice / Qualidade |
| 1:00 | 105 | 21 | 1.5 | 1 | 4 | 2 | 84 | 33 | 51 | 41 | 65 |
| 2:00 | 99 | 20 | 1.8 | 1.1 | 5 | 2 | 61 | 24 | 54 | 41 | 65 |
| 3:00 | 103 | 21 | 3.1 | 1.5 | 7 | 1 | 37 | 15 | 56 | 41 | 65 |
| 4:00 | 96 | 19 | 2.1 | 1.6 | 7 | 2 | 20 | 8 | 63 | 42 | 67 |
| 5:00 | 99 | 20 | -- | 1.7 | 8 | 2 | 10 | 4 | 68 | 43 | 68 |
| 6:00 | 99 | 20 | 2 | 1.8 | 8 | 1 | 5 | 2 | 67 | 44 | 70 |
| 7:00 | 97 | 20 | 1.4 | 1.9 | 8 | 5 | 2 | 1 | 65 | 46 | 73 |
| 8:00 | 97 | 20 | 1.1 | 1.9 | 8 | 20 | 4 | 2 | 69 | 47 | 75 |
| 9:00 | 102 | 20 | 1 | 1.8 | 8 | 59 | 12 | 5 | 63 | 48 | 76 |
| 10:00 | 83 | 17 | 1 | 1.7 | 8 | 125 | 27 | 11 | 64 | 48 | 76 |
| 11:00 | 27 | 6 | 0.6 | 1.3 | 6 | 173 | 48 | 19 | 58 | 49 | 78 |
| 12:00 | 22 | 4 | 0.5 | 1.1 | 5 | 192 | 72 | 29 | 44 | 49 | 78 |
| 13:00 | 15 | 3 | 0.4 | 1 | 4 | 206 | 98 | 39 | 34 | 50 | 79 |
| 14:00 | 17 | 3 | 0.5 | 0.8 | 4 | 234 | 127 | 75 | 32 | 50 | 79 |
| 15:00 | 20 | 4 | 0.6 | 0.7 | 3 | 246 | 157 | 115 | 50 | 51 | 82 |
| 16:00 | 23 | 5 | 0.7 | 0.7 | 3 | 258 | 187 | 173 | 69 | 52 | 83 |
| 17:00 | 27 | 5 | 0.7 | 0.6 | 3 | 261 | 212 | 205 | 81 | 54 | 86 |
| 18:00 | 60 | 12 | 0.9 | 0.6 | 3 | 196 | 221 | 208 | 93 | 56 | 90 |
| 19:00 | 69 | 14 | 0.8 | 0.6 | 3 | 101 | 212 | 205 | 63 | 56 | 90 |
| 20:00 | 78 | 15 | 0.9 | 0.7 | 3 | 76 | 197 | 193 | 36 | 56 | 90 |
| 21:00 | 44 | 9 | 0.7 | 0.7 | 3 | 117 | 186 | 171 | 15 | 55 | 88 |
| 22:00 | 42 | 8 | 0.7 | 0.7 | 3 | 103 | 170 | 140 | 26 | 55 | 86 |
| 23:00 | 49 | 10 | 0.7 | 0.8 | 3 | 96 | 151 | 108 | 38 | 54 | 86 |
| 24:00:00 | 47 | 9 | -- | 0.8 | 3 | 96 | 131 | 82 | 35 | 54 | 86 |

Ibirapuera - 13/10/2014

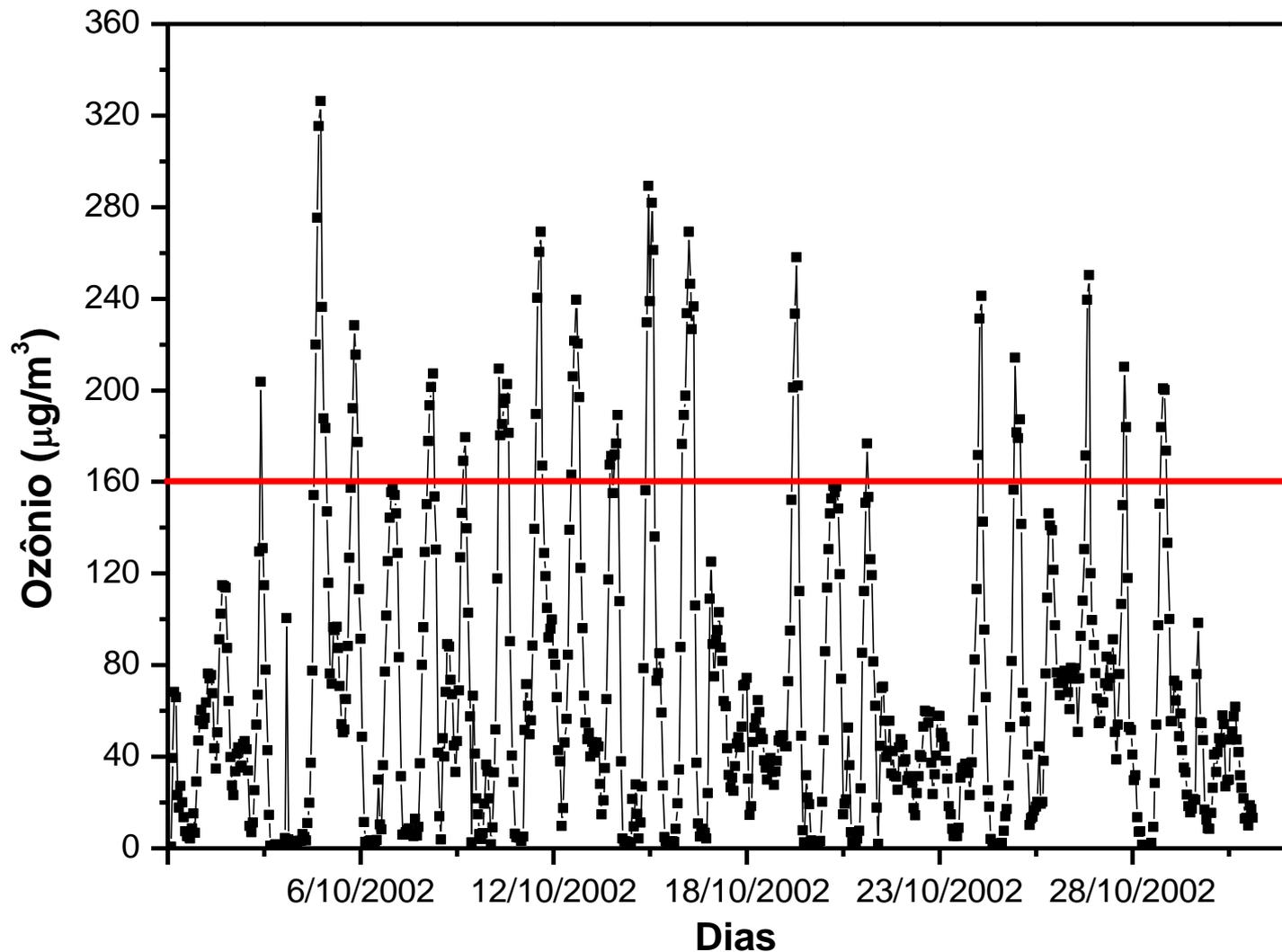
| Hora | NO2 µg/m ³ | | CO ppm | | | O3 µg/m ³ | | | MP2.5 µg/m ³ | | |
|-------|--------------------------|--------------------|---------------|-----------|--------------------|-------------------------|-----------|--------------------|----------------------------|------------|--------------------|
| | Média Horária | Índice / Qualidade | Média horária | Média 8 h | Índice / Qualidade | Média horária | Média 8 h | Índice / Qualidade | Média horária | Média 24 h | Índice / Qualidade |
| 1:00 | -- | -- | 1.5 | 1.4 | 6 | 18 | 54 | 21 | 80 | 53 | 85 |
| 2:00 | 59 | 12 | 1.2 | 1.5 | 7 | 40 | 41 | 16 | 80 | 55 | 88 |
| 3:00 | 66 | 13 | 1.3 | 1.5 | 7 | 26 | 26 | 10 | 64 | 55 | 88 |
| 4:00 | 68 | 14 | 1.3 | 1.5 | 7 | 21 | 19 | 8 | 44 | 54 | 86 |
| 5:00 | 56 | 11 | -- | 1.5 | 7 | 34 | 20 | 8 | 46 | 53 | 85 |
| 6:00 | 51 | 10 | 1.1 | 1.4 | 6 | -- | 21 | 8 | 69 | 55 | 88 |
| 7:00 | 64 | 13 | 1.2 | 1.3 | 6 | 26 | 24 | 10 | 22 | 54 | 86 |
| 8:00 | 90 | 18 | 1.5 | 1.3 | 6 | 20 | 27 | 11 | 60 | 55 | 88 |
| 9:00 | 116 | 23 | 1.6 | 1.3 | 6 | 37 | 29 | 12 | 91 | 55 | 88 |
| 10:00 | 97 | 19 | 1.4 | 1.3 | 6 | 90 | 36 | 14 | 92 | 55 | 88 |
| 11:00 | 38 | 8 | 0.9 | 1.3 | 6 | 157 | 55 | 22 | 86 | 55 | 88 |
| 12:00 | 23 | 5 | 0.7 | 1.2 | 5 | 182 | 78 | 31 | 79 | 54 | 86 |
| 13:00 | 19 | 4 | 0.7 | 1.1 | 5 | 199 | 102 | 43 | 59 | 53 | 85 |
| 14:00 | 20 | 4 | 0.7 | 1.1 | 5 | 204 | 114 | 59 | 34 | 53 | 85 |
| 15:00 | 21 | 4 | 0.8 | 1 | 4 | 231 | 140 | 93 | 46 | 52 | 83 |
| 16:00 | 25 | 5 | 0.8 | 0.9 | 4 | 241 | 168 | 136 | 67 | 53 | 85 |
| 17:00 | 25 | 5 | 0.9 | 0.9 | 4 | 235 | 192 | 183 | 51 | 53 | 85 |
| 18:00 | 39 | 8 | 1 | 0.8 | 4 | 189 | 205 | 202 | 56 | 52 | 83 |
| 19:00 | 66 | 13 | 1.2 | 0.8 | 4 | 108 | 199 | 197 | 24 | 52 | 83 |
| 20:00 | 78 | 16 | 1.3 | 0.9 | 4 | 69 | 185 | 169 | 26 | 53 | 85 |
| 21:00 | 53 | 11 | 1 | 0.9 | 4 | 93 | 171 | 142 | 4 | 53 | 85 |
| 22:00 | 44 | 9 | 0.9 | 1 | 4 | 112 | 160 | 119 | 25 | 53 | 85 |
| 23:00 | 50 | 10 | 0.9 | 1 | 4 | 97 | 143 | 97 | 35 | 54 | 86 |
| 24:00 | 62 | 12 | 1 | 1 | 4 | 68 | 121 | 68 | 16 | 52 | 83 |

Cid.Universitária-USP-Ipen - 14/10/2014

| Hora | NO2 µg/m³ | | CO ppm | | | O3 µg/m³ | | | MP2.5 µg/m³ | | |
|-------|---------------|--------------------|---------------|-----------|--------------------|----------------|-----------|--------------------|----------------|------------|--------------------|
| | Média Horária | Índice / Qualidade | Média horária | Média 8 h | Índice / Qualidade | Média horári a | Média 8 h | Índice / Qualidade | Média horári a | Média 24 h | Índice / Qualidade |
| 1:00 | 39 | 8 | 0.6 | 0.8 | 3 | 89 | 109 | 52 | 31 | 53 | 85 |
| 2:00 | 29 | 6 | 0.6 | 0.7 | 3 | 56 | 92 | 37 | 28 | 52 | 83 |
| 3:00 | 16 | 3 | 0.4 | 0.6 | 3 | 67 | 88 | 35 | 13 | 50 | 79 |
| 4:00 | 13 | 3 | 0.4 | 0.6 | 3 | 71 | 87 | 35 | 2 | 48 | 76 |
| 5:00 | 14 | 3 | -- | 0.6 | 2 | 70 | 81 | 32 | 10 | 45 | 71 |
| 6:00 | 27 | 5 | 0.4 | 0.5 | 2 | 45 | 74 | 29 | 10 | 43 | 68 |
| 7:00 | 43 | 9 | 0.5 | 0.5 | 2 | 37 | 66 | 26 | 12 | 41 | 65 |
| 8:00 | 51 | 10 | 0.7 | 0.5 | 2 | 36 | 59 | 23 | 21 | 39 | 62 |
| 9:00 | 48 | 10 | 0.9 | 0.5 | 2 | 53 | 54 | 21 | 19 | 37 | 59 |
| 10:00 | 57 | 11 | 0.8 | 0.6 | 3 | 61 | 55 | 22 | 24 | 35 | 56 |
| 11:00 | 22 | 5 | 0.6 | 0.6 | 3 | 90 | 58 | 23 | 31 | 34 | 54 |
| 12:00 | 20 | 4 | 0.5 | 0.6 | 3 | 106 | 62 | 25 | 22 | 33 | 53 |
| 13:00 | 32 | 6 | 0.6 | 0.6 | 3 | 146 | 72 | 29 | 17 | 32 | 51 |
| 14:00 | 40 | 8 | 0.7 | 0.6 | 3 | 190 | 90 | 36 | 27 | 32 | 51 |
| 15:00 | 57 | 11 | 0.9 | 0.7 | 3 | 267 | 119 | 65 | 38 | 32 | 51 |
| 16:00 | 66 | 13 | 0.9 | 0.7 | 3 | 289 | 150 | 106 | 60 | 31 | 50 |
| 17:00 | 63 | 12 | 1 | 0.8 | 3 | 316 | 183 | 165 | 66 | 31 | 50 |
| 18:00 | 66 | 13 | 1.1 | 0.8 | 3 | 299 | 213 | 205 | 65 | 30 | 48 |
| 19:00 | 122 | 24 | 1.4 | 0.9 | 4 | 185 | 225 | 209 | 59 | 29 | 46 |
| 20:00 | 140 | 28 | 1.7 | 1 | 4 | 151 | 230 | 211 | 57 | 30 | 48 |
| 21:00 | 127 | 26 | 1.5 | 1.1 | 5 | 102 | 225 | 209 | 77 | 33 | 53 |
| 22:00 | 52 | 11 | 0.8 | 1.1 | 5 | 90 | 212 | 205 | 53 | 34 | 54 |
| 23:00 | 39 | 8 | 0.6 | 1.1 | 5 | 84 | 190 | 179 | 43 | 34 | 54 |
| 24:00 | 25 | 5 | 0.5 | 1 | 5 | 75 | 163 | 126 | 32 | 34 | 54 |

Cid.Universitária-USP-Ipen - 15/10/2014

| Hora | NO2 µg/m ³ | | CO ppm | | | O3 µg/m ³ | | | MP2.5 µg/m ³ | | |
|-------|--------------------------|--------------------|---------------|-----------|--------------------|-------------------------|-----------|--------------------|----------------------------|------------|--------------------|
| | Média Horária | Índice / Qualidade | Média horária | Média 8 h | Índice / Qualidade | Média horária | Média 8 h | Índice / Qualidade | Média horária | Média 24 h | Índice / Qualidade |
| 1:00 | 15 | 3 | 0.4 | 1 | 4 | 86 | 134 | 86 | 25 | 34 | 54 |
| 2:00 | 8 | 2 | 0.3 | 0.9 | 4 | 102 | 109 | 52 | 24 | 34 | 54 |
| 3:00 | 10 | 2 | 0.3 | 0.8 | 3 | 96 | 98 | 39 | 21 | 34 | 54 |
| 4:00 | 13 | 3 | 0.4 | 0.6 | 3 | 95 | 91 | 36 | 30 | 35 | 56 |
| 5:00 | 16 | 3 | -- | 0.5 | 2 | 97 | 91 | 36 | 37 | 36 | 57 |
| 6:00 | 17 | 3 | 0.6 | 0.4 | 2 | 87 | 90 | 36 | 34 | 37 | 59 |
| 7:00 | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- | -- |
| 8:00 | 41 | 8 | 1.2 | 0.5 | 2 | 72 | 91 | 36 | 8 | 38 | 61 |
| 9:00 | 38 | 8 | 1.3 | 0.7 | 3 | 103 | 93 | 37 | 13 | 37 | 59 |
| 10:00 | 35 | 7 | 1.1 | 0.8 | 4 | 123 | 96 | 38 | 24 | 37 | 59 |
| 11:00 | 32 | 6 | 1.1 | 0.9 | 4 | 114 | 99 | 39 | 38 | 38 | 61 |
| 12:00 | 31 | 6 | 1.1 | 1.1 | 5 | 147 | 106 | 48 | 42 | 39 | 62 |
| 13:00 | 28 | 6 | 1 | 1 | 4 | 122 | 110 | 53 | 43 | 40 | 64 |
| 14:00 | 21 | 4 | 1 | 1.1 | 5 | 96 | 111 | 55 | 37 | 40 | 64 |
| 15:00 | 21 | 4 | 1 | 1.1 | 5 | 89 | 108 | 51 | 38 | 40 | 64 |
| 16:00 | 28 | 6 | 1.1 | 1.1 | 5 | 73 | 108 | 51 | 38 | 39 | 62 |
| 17:00 | 35 | 7 | 1.4 | 1.1 | 5 | 59 | 103 | 44 | 34 | 38 | 61 |
| 18:00 | 32 | 6 | 1.4 | 1.1 | 5 | 59 | 95 | 38 | 35 | 37 | 59 |
| 19:00 | 36 | 7 | 1.5 | 1.2 | 5 | 52 | 87 | 35 | 32 | 35 | 56 |
| 20:00 | 23 | 5 | 1.4 | 1.2 | 5 | 69 | 77 | 31 | 35 | 34 | 54 |
| 21:00 | 21 | 4 | 1.3 | 1.3 | 6 | 68 | 71 | 28 | 22 | 32 | 51 |
| 22:00 | 25 | 5 | 1.4 | 1.3 | 6 | 67 | 67 | 27 | 16 | 31 | 48 |
| 23:00 | 22 | 5 | 1.3 | 1.4 | 6 | 74 | 65 | 26 | 21 | 30 | 48 |
| 24 | 18 | 3 | 1.3 | 1.4 | 6 | 75 | 65 | 26 | 19 | 29 | 46 |



Concentração média horária de ozônio no mês de outubro de 2002, na estação Ibirapuera da CETESB. A linha vermelha corresponde ao PQAR ($160 \mu\text{g m}^{-3}$).

Smog fotoquímico → ozônio troposférico

Precursores: compostos orgânicos voláteis (COVs) e NO_x ($\text{NO} + \text{NO}_2$).

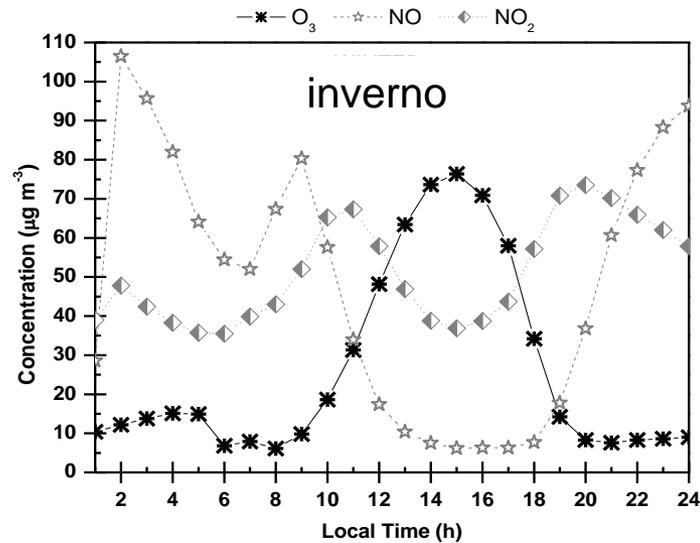
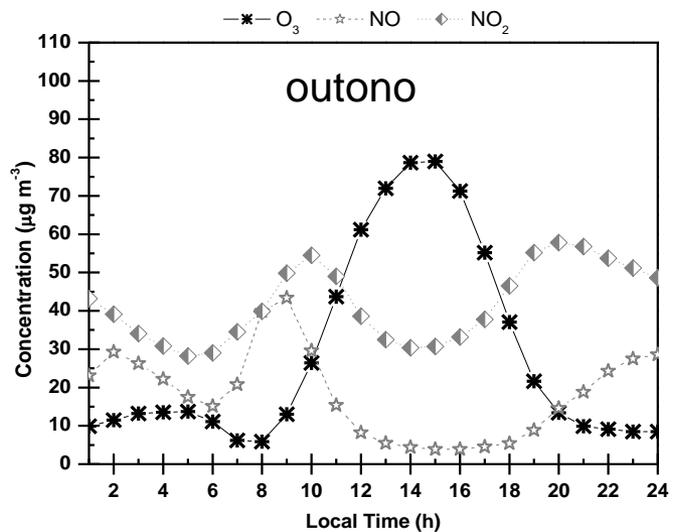
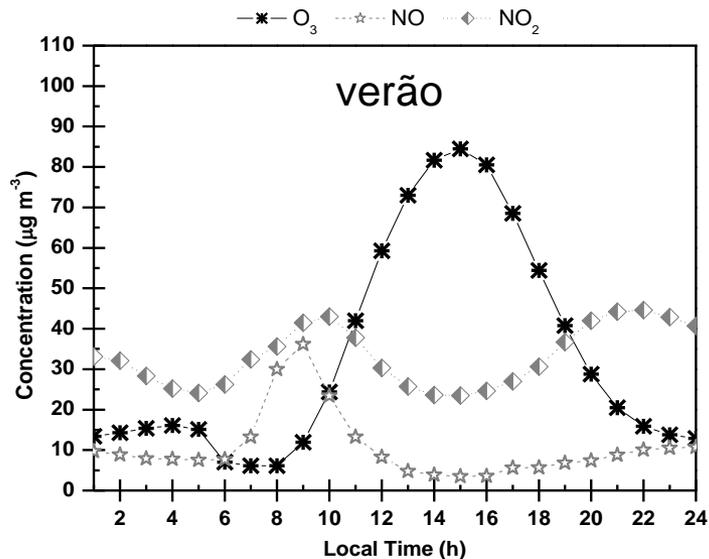
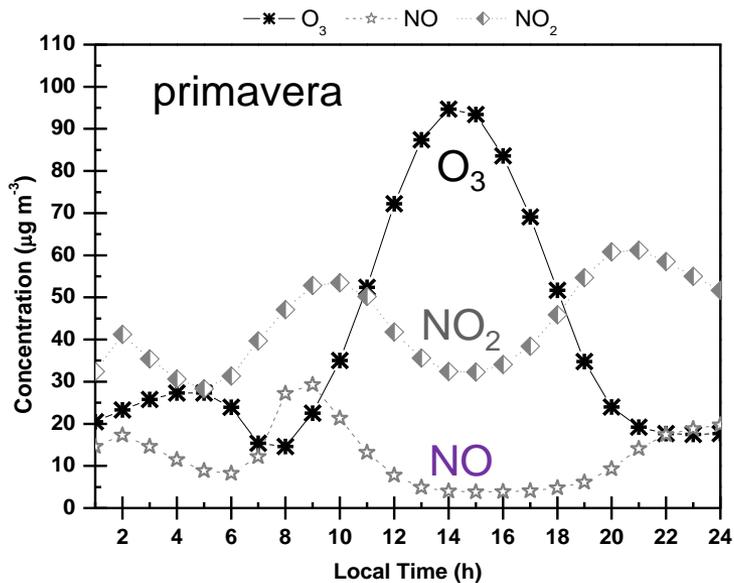
Função não linear de fatores :

- temperatura do ar,
- espectro e intensidade da radiação solar,
- mistura atmosférica e outros parâmetros meteorológicos,
- as concentrações dos precursores, razão COVs/NO_x e
- reatividade dos precursores orgânicos.

Reações entre poluentes e constituintes gasosos naturais do ar catalisadas por luz solar.

Aparece como bruma castanha ou cinza nas áreas urbanas; reações fotoquímicas são comuns em áreas urbanas onde a radiação solar é muito intensa.

Perfil horário da concentração horária sazonal para NO, NO₂ e O₃ medidos pela CETESB (Ibirapuera: janeiro de 2002 a dezembro de 2007).



Razão COV/NO_x

Importância para produção de ozônio troposférico

Os **compostos orgânicos voláteis (COVs)** podem ser definidos a partir de suas propriedades físico-químicas, ou seja, compostos que a 20°C apresentam pressão de vapor igual ou maior do 0,01 kPa (European Union, EC Directive 1999/13/EC).

Porém, os COVs também são caracterizados como os compostos orgânicos que contribuem (reatividade) para a formação fotoquímica do ozônio.

Também podem ter impacto negativo à saúde humana, seja diretamente pela toxicidade individual de alguns compostos ou indiretamente a partir da formação de oxidantes atmosféricos e mesmo material particulado orgânico secundário (SOA, *secondary organic aerosol*).

Definições de COVs

A definição de COVs varia de acordo com o contexto. Uma definição muito geral é “COVs são substâncias orgânicas que são voláteis e são fotoquimicamente reativas”. Abaixo estão as definições de VOCs usadas por várias organizações.

UNECE (Comissão Económica das Nações Unidas para a Europa):

Todos os compostos orgânicos de natureza antropogênica, com exceção do metano, que são capazes de produzir oxidantes fotoquímicos reagindo com óxidos de nitrogênio na presença de luz solar são COVs.

OMS (Organização Mundial da Saúde):

A Organização Mundial da Saúde definiu COV com base na faixa de 'Ponto de ebulição', "qualquer composto orgânico" será denotado como composto orgânico muito volátil (VVOC) se o ponto de ebulição estiver na faixa de $< 0^{\circ} \text{C}$ a até 50°C ; e será denotado como composto orgânico volátil (COV) se o ponto de ebulição estiver na faixa de $50^{\circ} \text{C} - 100^{\circ} \text{C}$ até $240 - 260^{\circ} \text{C}$.

ASTM (organização internacional de desenvolvimento de padrões):

Qualquer composto de carbono evaporando sob condições de teste específicas; água e solventes voláteis isentos (cloro de metileno, p-clorobenzotrifluoreto, acetona, metil siloxanos voláteis) não estão incluídos como VOC.

ISO 16000-6 (Organização Internacional para Padronização):

Qualquer composto orgânico no ar interno de residências, escritórios e prédios públicos, bem como compostos orgânicos, emitidos a partir de materiais de construção e são detectados na câmara de teste”. **Esta definição refere-se à Qualidade do Ar Interior.**

União Europeia (Diretiva 2001/81/EC):

"compostos orgânicos voláteis" e "COV" significam todos os compostos orgânicos resultantes de atividades humanas, com exceção do metano, que são capazes de produzir oxidantes fotoquímicos por reações com óxidos de nitrogênio na presença de luz solar".

Definição da EPA dos EUA de Compostos Orgânicos Voláteis

"Compostos orgânicos voláteis (COVs)" significa qualquer composto de carbono, excluindo monóxido de carbono, dióxido de carbono, ácido carbônico, carbonetos ou carbonatos metálicos e carbonato de amônio, que participa de reações fotoquímicas atmosféricas.

Os COVs podem ser encontrados desde regiões remotas até áreas rurais e ambientes altamente urbanizados.

A principal fonte são as emissões biogênicas (BCOVs), sendo a estimativa da emissão global de isopreno (C_5H_{10}) na ordem de 500 TgC/ano seguido dos terpenos ($C_{10}H_{16}$) com emissões acima de 120 TgC/ano (IPCC, 2013).

Além de isopreno e terpenos as emissões biogênicas incluem alcanos, alcenos, alcoóis, ésteres, carbonilas e ácidos (Kesselmeier e Staudt, 1999).

Dentre todos os COVs, benzeno, tolueno, etilbenzeno e xilenos (BTEX) são os mais monitorados por estarem presentes em praticamente todo ambiente urbano moderno, muitas vezes em concentrações relativamente altas, assim como por serem classificados como carcinogênicos ou potencialmente carcinogênicos para humanos (Do et al., 2013 e Makar et al., 2003).

Hidrocarbonetos

1 a 4 carbonos \Rightarrow gases

> número de carbonos \Rightarrow líquidos ou sólidos no estado puro

< 8 carbonos \Rightarrow são os mais abundantes

> 12 carbonos \Rightarrow pequenas quantidades na atmosfera

Alcanos (ou parafinas ou alifáticos) $\Rightarrow C_nH_{2n+2}$

Alcenos (olefinas) $\Rightarrow C_nH_{2n}$

Alcinos $\Rightarrow C_nH_{2n-2}$ (acetileno, $HC \equiv CH$, emitido predominantemente por veículos)

Terpenos $\Rightarrow C_{10}H_{16}$ (emitidos pela vegetação. Ex: isopreno, C_5H_8)

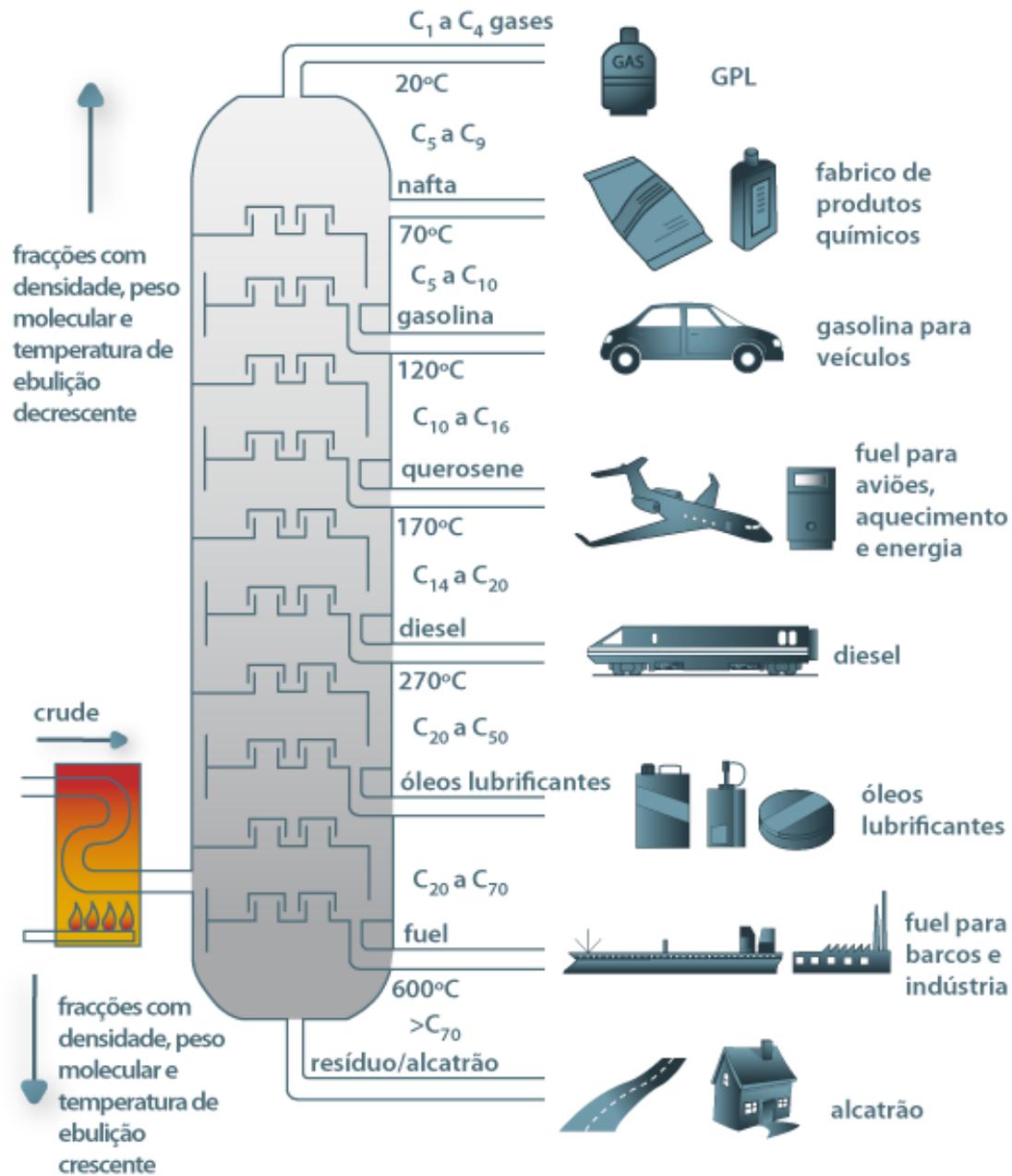
Hidrocarbonetos

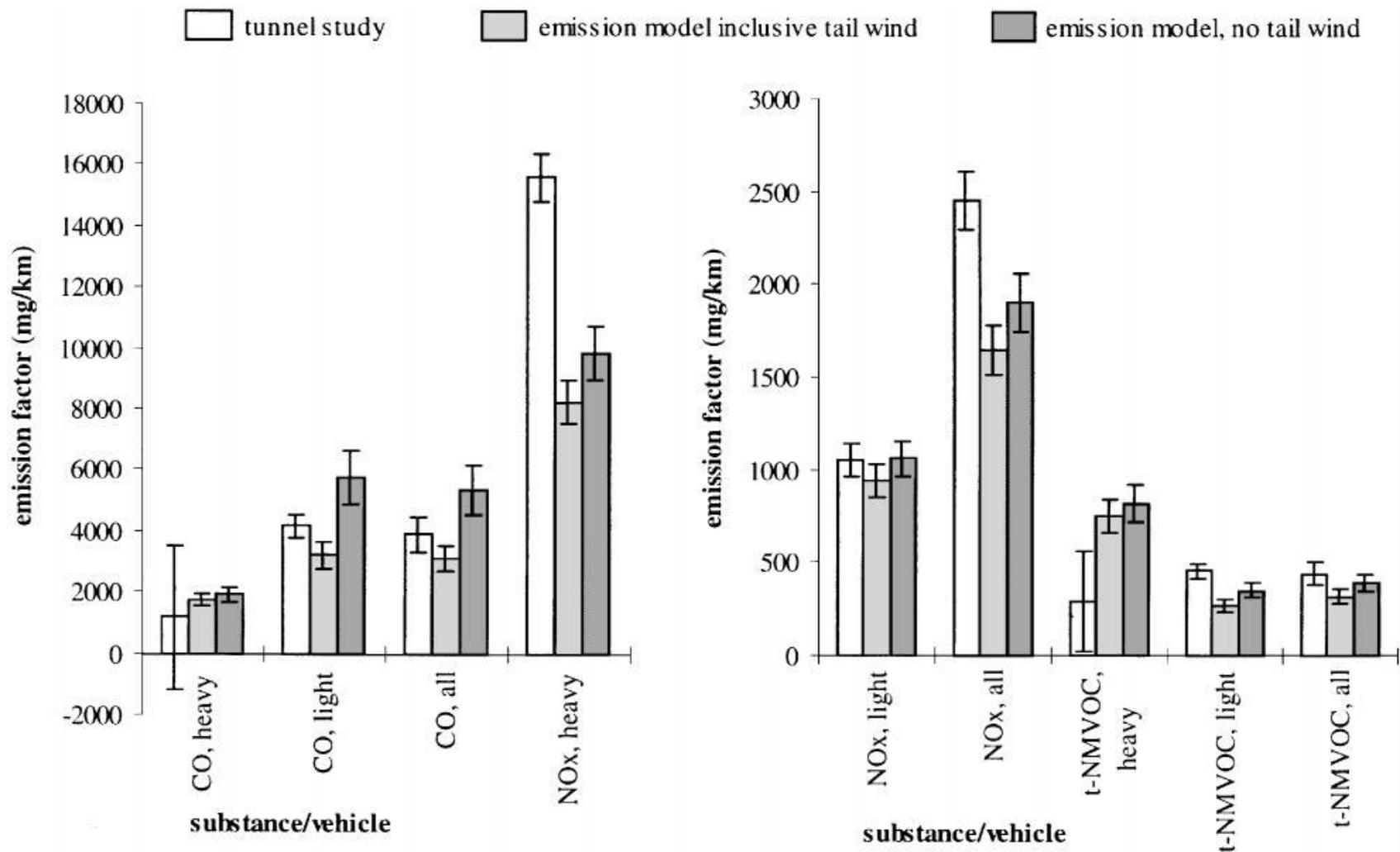
Produtos do Petróleo

| | | |
|-------------|------------------------------|---------------------|
| Metano | CH_4 | Gás natural |
| Etano | C_2H_6 | |
| Propano | C_3H_8 | GPL |
| Butano | C_4H_{10} | |
| Pentano | C_5H_{12} | Éter de petróleo |
| Hexano | C_6H_{14} | |
| Heptano | C_7H_{16} | Gasolina |
| Octano | C_8H_{18} | |
| Nonano | C_9H_{20} | |
| Decano | $\text{C}_{10}\text{H}_{22}$ | |
| Undecano | $\text{C}_{11}\text{H}_{24}$ | |
| Dodecano | $\text{C}_{12}\text{H}_{26}$ | Querosene |
| Tridecano | $\text{C}_{13}\text{H}_{28}$ | |
| Tetradecano | $\text{C}_{14}\text{H}_{30}$ | Diesel |
| Pentadecano | $\text{C}_{15}\text{H}_{32}$ | |
| Hexadecano | $\text{C}_{16}\text{H}_{34}$ | Óleos lubrificantes |
| Heptadecano | $\text{C}_{17}\text{H}_{36}$ | |
| Octadecano | $\text{C}_{18}\text{H}_{38}$ | Petrolatum |
| Nonadecano | $\text{C}_{19}\text{H}_{40}$ | |
| Ecosano | $\text{C}_{20}\text{H}_{42}$ | Alcatrão |

O Éter de Petróleo é uma mistura de hidrocarbonetos pentano (C_5H_{12}) e hexano (C_6H_{14}), utilizado como solvente em laboratórios, indústrias, tinturarias, em lavagens a seco, como desengraxante e na remoção de adesivos.

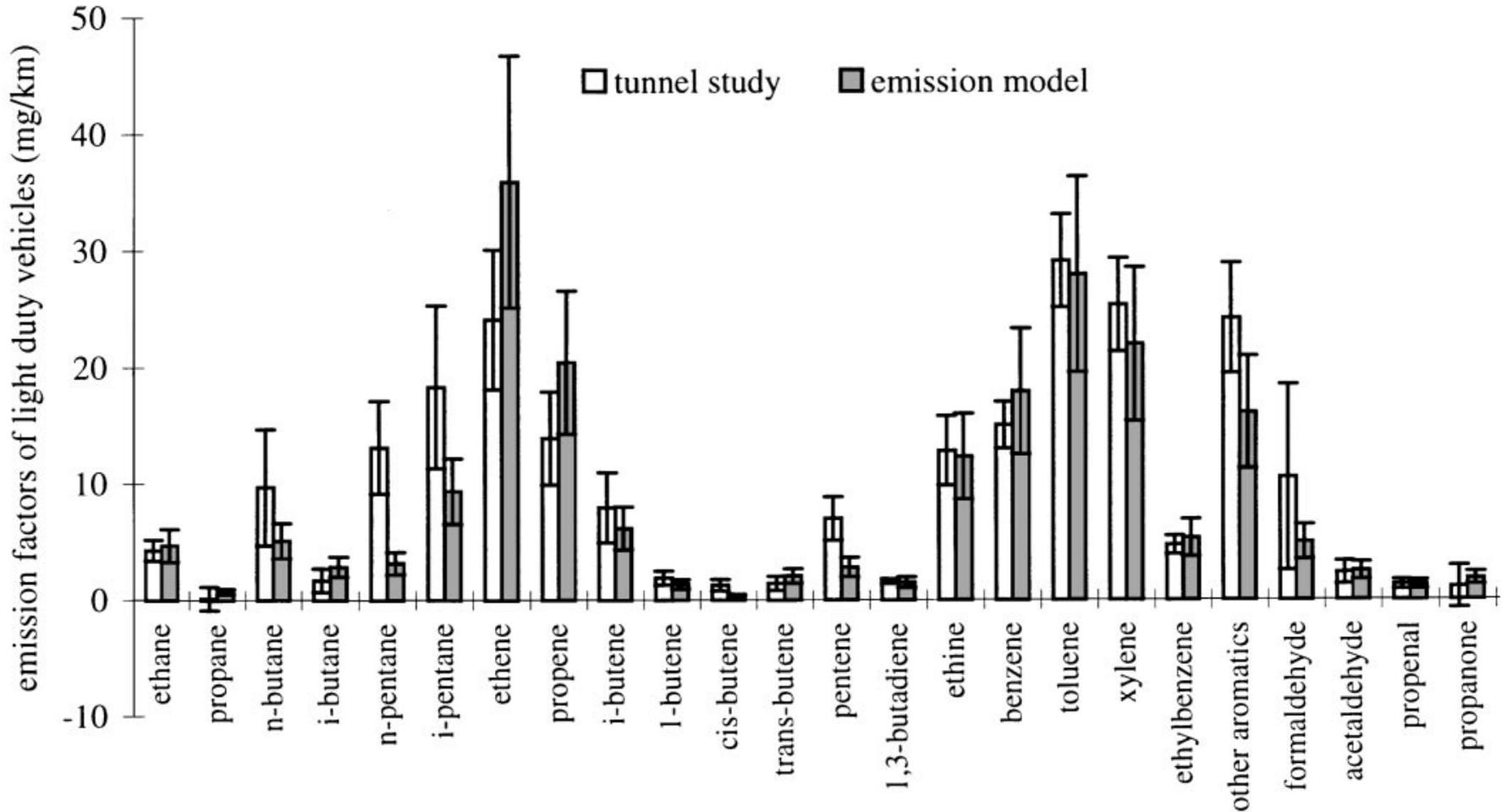
Não é Éter Etílico ($\text{C}_2\text{H}_5\text{--O--C}_2\text{H}_5$). A coincidência de nomes é devida à alta volatilidade desses hidrocarbonetos (semelhante a do Éter Etílico).





Comparação de EF de NO_x, NMVOC total e CO. O modelo de emissão utiliza resultados de testes dinamométricos. Os testes em túnel de vento é simulado reduzindo a inclinação da subida.

Exemplo de emissão de hidrocarbonetos por queima de gasolina

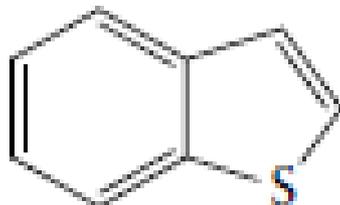


Comparação dos fatores de emissão de veículos leves para hidrocarbonetos individuais (John et al., Comparison of emission factors for road traffic from a tunnel study (Gubrist tunnel, Switzerland) and from emission modeling, Atmospheric Environment 33,1999, 3367-3376).

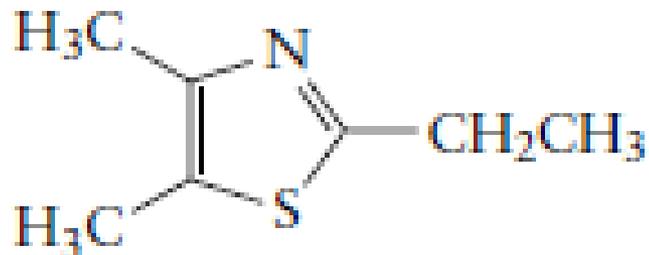
Petróleo contém enxofre (0,1 até 3,7% em peso) em compostos chamados tiofenos. Quando os derivados de petróleo são queimados o enxofre é emitido na forma de dióxido de enxofre (SO₂).



Thiophene



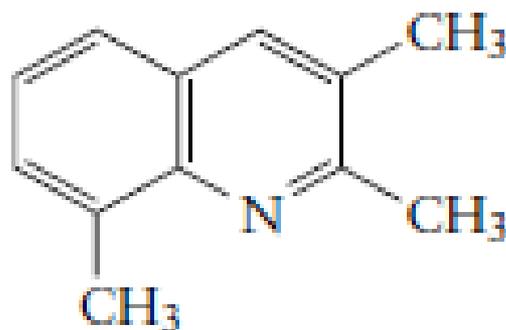
2,3-Benzothiophene



2-Ethyl-4,5-dimethylthiazole

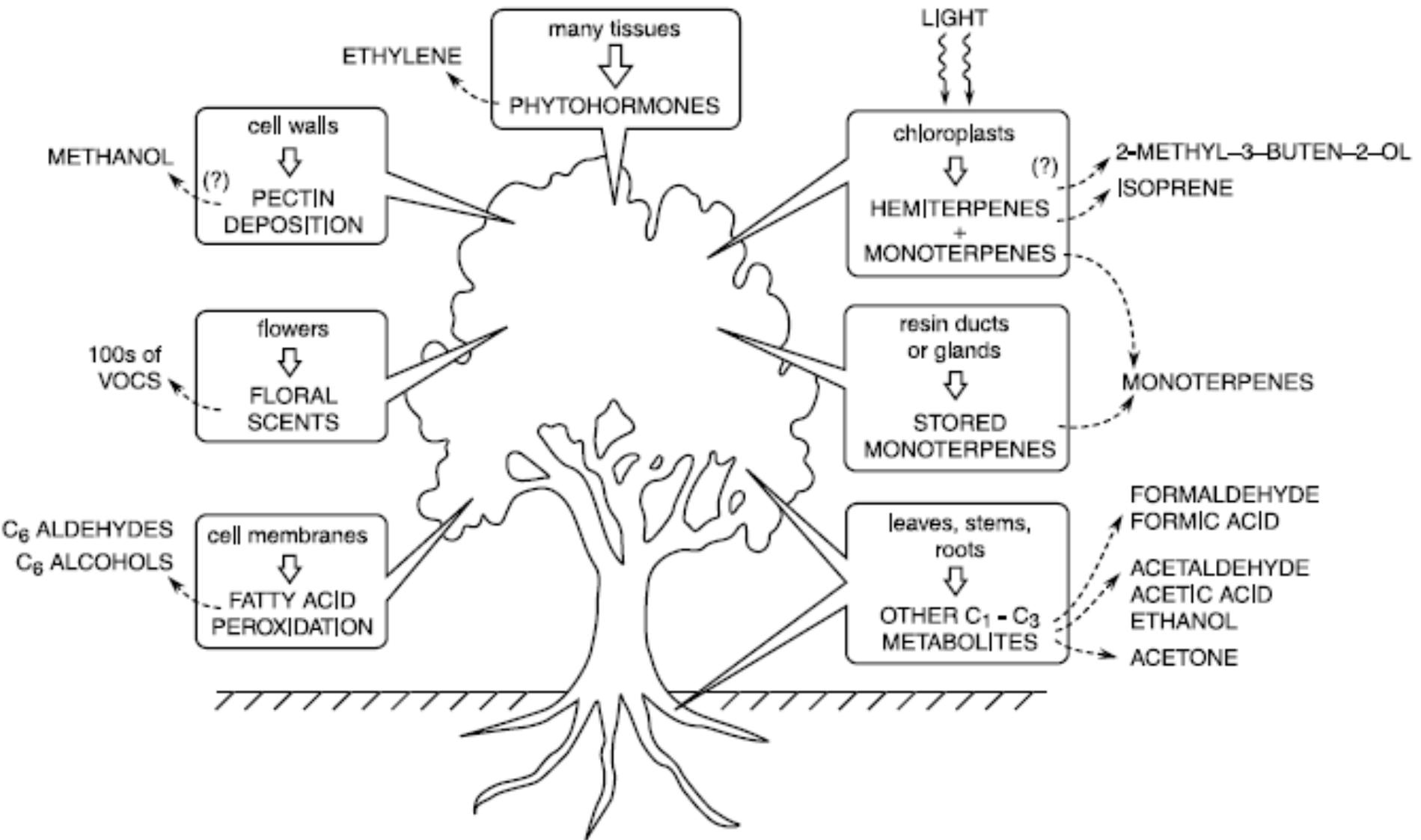


Thiazole



2,3,8-Trimethylquinoline

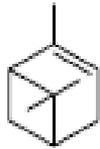
COV – emissões biogênicas



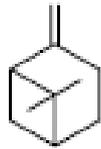


Isoprene

Hemiterpeno C₅H₁₀

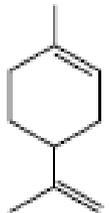


α -Pinene



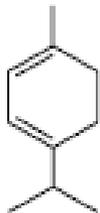
β -Pinene

Estrutura química de alguns hidrocarbonetos originados da emissão biogênica

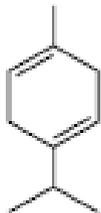


Limonene

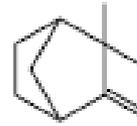
Monoterpenos C₁₀H₁₆



α -Terpinene



γ -Terpinene



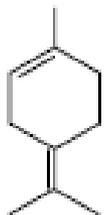
Camphene

TABLE 6.24 Estimated Global Annual Biogenic VOC Emissions (Tg yr⁻¹)^a

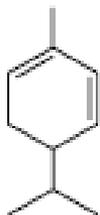
| Source | Isoprene | Monoterpenes | Other VOCs ^b |
|---|-------------|--------------|-------------------------|
| Canopy foliage | 460 | 115 | 500 |
| Terrestrial ground cover and soils | 40 | 13 | 50 |
| Flowers | 0 | 2 | 2 |
| Ocean and freshwater | 1 | <0.001 | 10 |
| Animals, humans, and insects | 0.003 | <0.001 | 0.003 |
| Anthropogenic (including biomass burning) | 0.01 | 1 | 93 |
| Total | ~500 | ~130 | ~650 |

^a From Guenther (1999) and references therein.

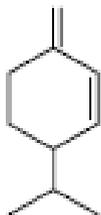
^b Other VOCs include all volatile organic compounds other than methane, isoprene, and monoterpenes.



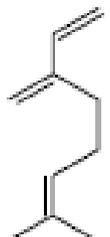
Terpinolene



α -Phellandrene



β -Phellandrene



Myrcene



Ocimene



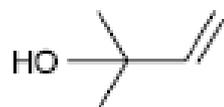
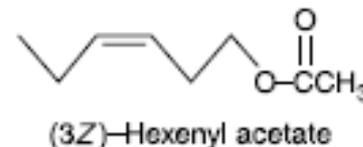
Δ^3 -Carene



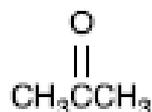
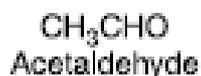
p-Cymene

Cimeno é um alquilbenzeno relacionado aos Monoterpenos C₁₀H₁₄

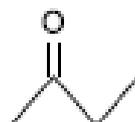
Estrutura química de alguns compostos oxigenados orgânicos originados da emissão biogênica



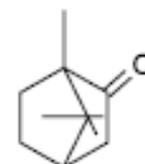
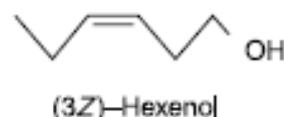
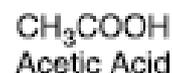
2-Methyl-3-buten-2-ol



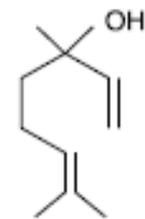
Acetone



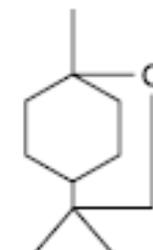
Butanone



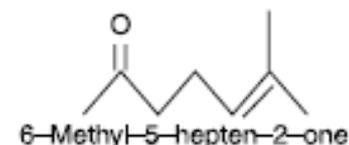
Camphor



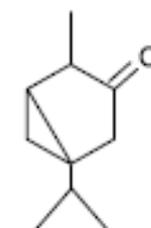
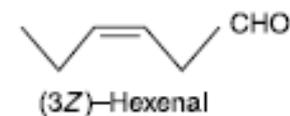
Linalool



1,8-Cineol



6-Methyl-5-hepten-2-one

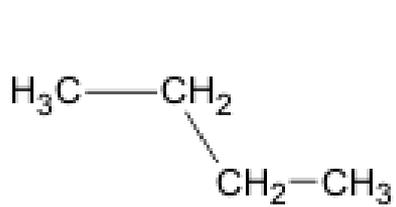


Thujone

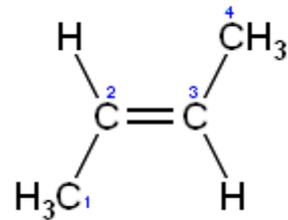
Estimativas de tempo de vida de alguns COVs representativos na troposfera.

| Organic | OH ($1 \times 10^6 \text{ cm}^{-3}$) | O ₃ (100 ppb) | NO ₃ (50 ppt) | Cl ($1 \times 10^4 \text{ cm}^{-3}$) |
|------------------------|---|-----------------------------|-----------------------------|---|
| <i>n</i> -Butane | 5 days | ≥ 1300 yr | 205 days | 5 days |
| <i>trans</i> -2-Butene | 4.3 h | 36 min | 35 min | ~4 days |
| Acetylene | 14 days | ≥ 400 days | ≥ 188 days | ~22 days ^c |
| Toluene | 2 days | ≥ 400 days | 138 days ^d | 20 days |
| HCHO | 1.2 days | ≥ 463 days | 16 days | 16 days |

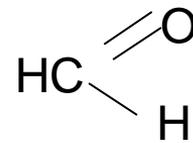
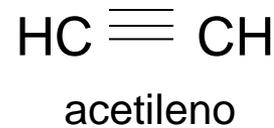
Pg. 181, Finlayson – Pitts & Pitts, 2000



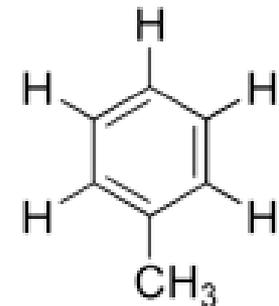
n-butano



trans 2-buteno



formaldeído



tolueno

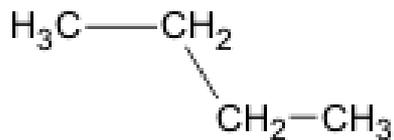
Principal oxidante de COVs

Estimativas de tempo de vida de alguns COVs representativos na troposfera.

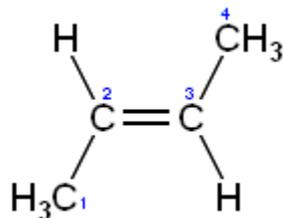
| Organic | OH ($1 \times 10^6 \text{ cm}^{-3}$) | O ₃ (100 ppb) | NO ₃ (50 ppt) | Cl ($1 \times 10^4 \text{ cm}^{-3}$) |
|------------------------|---|-----------------------------|-----------------------------|---|
| <i>n</i> -Butane | 5 days | ≥ 1300 yr | 205 days | 5 days |
| <i>trans</i> -2-Butene | 4.3 h | 36 min | 35 min | ~4 days |
| Acetylene | 14 days | ≥ 400 days | ≥ 188 days | ~22 days ^c |
| Toluene | 2 days | ≥ 400 days | 138 days ^d | 20 days |
| HCHO | 1.2 days | ≥ 463 days | 16 days | 16 days |

Importante na MBL (marine boundary layer)

Pg. 181, Finlayson – Pitts & Pitts, 2000

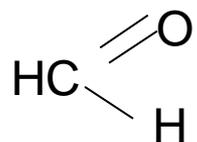
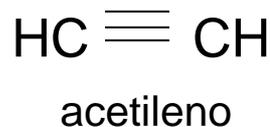


n-butano

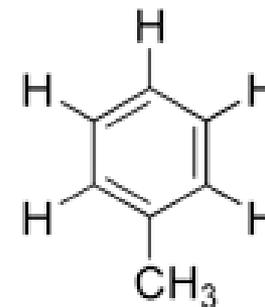


trans 2-buteno

Importante:
reações de ozônio
com alcenos!!!



formaldeído



tolueno

Tempo de vida de alguns compostos na troposfera livre (nível do mar)

Lifetime in free-tropospheric air at sea level

| ROG Species | Photolysis | [OH] | [HO ₂] | [O] | [NO ₃] | [O ₃] |
|------------------------|------------|--|--|--|--|---|
| | | 5×10^5 molec. cm ⁻³ | 3×10^8 molec. cm ⁻³ | 3×10^3 molec. cm ⁻³ | 5×10^8 molec. cm ⁻³ | 1×10^{12} molec. cm ⁻³ |
| <i>n</i> -Butane | – | 9.2 d | 6700 y | 480 y | 1.6 y | 3250 y |
| <i>trans</i> -2-Butene | – | 8.7 h | 27 y | 168 d | 1.3 h | 1.4 h |
| Acetylene | – | 30 d | – | 67 y | – | 2.7 y |
| Toluene | – | 3.8 d | – | 160 y | 1.8 y | 2.7 y |
| Isoprene | – | 5.7 h | – | 106 d | 1.7 h | 23 d |
| Formaldehyde | 7 h | 2.5 d | 11.7 h | 67 y | 40 d | 16,000 y |
| Acetone | 23 d | 96 d | – | – | – | – |

Comparação entre os tempos de vida de **alcanos** em função de reações com diferentes oxidantes atmosféricos: OH, NO₃, Cl, Br e O₃

| Hydrocarbon | $k, \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ | | | | | | | | | |
|------------------------|--|--------|------------------------|------------------|--------------------|--------|----------------------|---------------------------------|--------------------|-------------------|
| | OH | | NO ₃ | | Cl | | Br | | O ₃ | |
| | $k \times 10^{12}$ | τ | $k \times 10^{12}$ | τ | $k \times 10^{10}$ | τ | $k \times 10^{12}$ | τ | $k \times 10^{18}$ | τ |
| <i>Alkanes</i> | | | | | | | | | | |
| Ethane | 0.24 | 48 d | $< 1.0 \times 10^{-5}$ | $> 13 \text{ y}$ | 0.57 | 6.7 mo | 3.1×10^{-7} | $1.0 \times 10^6 \text{ y}^2$ | < 0.01 | $> 3.2 \text{ y}$ |
| Propane | 1.1 | 11 d | 0.00021 | > 0.60 | 1.3 | 90 d | 0 | $6.5 \times 10^3 \text{ y}^2$ | < 0.01 | $> 3.2 \text{ y}$ |
| 2-Methylpropane | 2.1 | 5.6 d | < 0.00007 | $> 18 \text{ y}$ | 1.3 | 90 d | $< 1.0 \times$ | $> 3.2 \times 10^7 \text{ y}^2$ | < 0.01 | $> 3.2 \text{ y}$ |
| <i>n</i> -Butane | 2.3 | 5.2 d | 0.000046 | 2.8 y | 2.3 | 50 d | $< 1.0 \times$ | $> 3.2 \times 10^7 \text{ y}^2$ | < 0.01 | $> 3.2 \text{ y}$ |
| 2-Methylbutane | 4 | 2.9 d | 0.00016 | 0.79 y | 2 | 60 d | NA | NA | NA | NA |
| <i>n</i> -Pentane | 3.8 | 3.0 d | 0.000081 | 1.6 y | 2.5 | 46 d | NA | NA | NA | NA |
| 2,2-Dimethylbutane | 2.7 | 4.3 d | NA | NA | NA | NA | NA | NA | NA | NA |
| 2,3-Dimethylbutane | 6.4 | 1.8d | 0.00041 | 110 d | 2 | 60 d | 0.0064 | 50 y | NA | NA |
| 2-Methylpentane | 5.6 | 2.1 d | 0.000017 | 7.5 y | 2.5 | 47 d | NA | NA | NA | NA |
| 3-Methylpentane | 5.8 | 2.0 d | 0.00002 | 6.3 y | 2.5 | 46d | NA | NA | NA | NA |
| <i>n</i> -Hexane | 5.2 | 2.2 d | 0.00011 | 1.2 y | 3.1 | 38 d | NA | NA | NA | NA |
| 2,2,4-Trimethylpentane | 3.8 | 3.0 d | 0.000075 | 1.7 y | 2.3 | 50 d | 0.0068 | 47 y | NA | NA |

Comparação entre os tempos de vida de **alcenos** em função de reações com diferentes oxidantes atmosféricos: OH, NO₃, Cl, Br e O₃

| Hydrocarbon | $k, \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ | | | | | | | | | |
|---------------------------|---|--------|--------------------|--------|--------------------|--------|--------------------|--------|--------------------|--------|
| | OH | | NO ₃ | | Cl | | Br | | O ₃ | |
| | $k \times 10^{12}$ | τ | $k \times 10^{12}$ | τ | $k \times 10^{10}$ | τ | $k \times 10^{12}$ | τ | $k \times 10^{18}$ | τ |
| <i>Alkenes</i> | | | | | | | | | | |
| Ethene | 8.5 | 33 h | 0 | 230 d | 0.99 | 3.8 m | 0.18 | 1.8 y | 1.6 | 7.2 d |
| Propene | 26 | 11 h | 0.01 | 4.9 d | 2.3 | 50 d | 5.3 | 22 d | 10 | 1.2 d |
| 2-Methylpropene | 51 | 5.4 h | 0.34 | 3.3 h | 0.42 | 9.0 m | NA | NA | 11 | 1.1 d |
| 1-Butene | 31 | 9.0 h | 0.013 | 3.6 d | 1.4 | 65 d | 3.4 | 34 d | 9.6 | 1.2 d |
| <i>trans</i> -2-Butene | 64 | 4.3 h | 0.39 | 2.8 h | NA | NA | 0.23 | 1.4 y | 190 | 1.5 h |
| <i>cis</i> -2-Butene | 56 | 5.0 h | 0.35 | 3.2 h | NA | NA | 6.3 | 18 d | 125 | 2.3 h |
| 1,3-Butadiene | 67 | 4.1 h | 0.1 | 11 h | 4.2 | 28 d | 57 | 2.0 d | 6.3 | 1.8 d |
| Isoprene | 100 | 2.8 h | 0.68 | 1.6 h | 5.1 | 23 d | 74 | 1.6 d | 13 | 21 h |
| 2-Methyl-2-butene | 87 | 3.2 h | 9.4 | 0.12 h | NA | NA | 19 | 6.1 d | 400 | 0.69 h |
| 1-Pentene | 31 | 9.0 h | 0.7 | 1.6 h | NA | NA | NA | NA | 11 | 1.1 d |
| <i>trans</i> -2-Pentene | 67 | 4.1 h | 1.6 | 0.69 h | NA | NA | NA | NA | 320 | 0.86 h |
| <i>cis</i> -2-Pentene | 65 | 4.3 h | 1.4 | 0.79 h | NA | NA | NA | NA | 210 | 1.3 h |
| 2,4,4-Trimethyl-1-pentene | 65 | 4.3 h | 0.51 | 2.2 h | NA | NA | NA | NA | NA | NA |

Notes: NA = Reaction rate coefficient not available. Rate coefficients were calculated at 298K and 1 atmosphere. y = year. d = day.
 OH = $1 \times 10^6/\text{cm}^3$; NO₃ = $2.5 \times 10^9/\text{cm}^3$; Cl = $1 \times 10^3/\text{cm}^3$; Br = $1 \times 10^3/\text{cm}^3$; O₃ = $1 \times 10^{12}/\text{cm}^3$. Value for BR calculated based on equilibrium with BrO = 1 ppt.

¹ Rate Coefficients were Obtained from the NIST Online Kinetics Database for Reactions of Alkanes and for all Cl and Br Reactions.

All Other Rate Coefficients were Obtained from the Evaluation of Calvert et al. (2000).

² Lifetimes should be regarded as lower limits.

Sources: NIST online kinetics database (<http://kinetics.nist.gov/index.php>).

EPA, 2005

Reações de hidrocarbonetos na atmosfera

Emissões de hidrocarbonetos incluem fontes naturais (vegetação), e antropogênicas (queima de combustíveis fósseis, processos industriais).

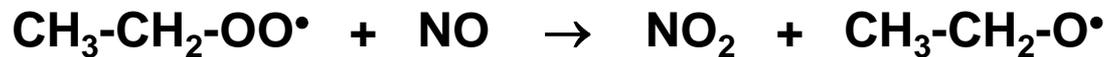
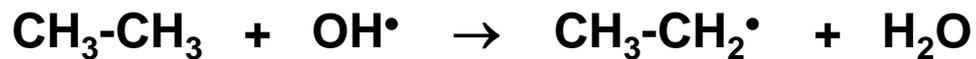
Material orgânico na atmosfera é decomposto principalmente via radical hidroxila, que em atmosfera não poluída é formado através da reação de decomposição do ozônio pela radiação UV, formando oxigênio atômico e oxigênio singlete, que é extremamente reativo:



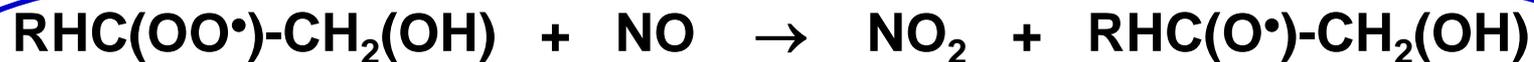
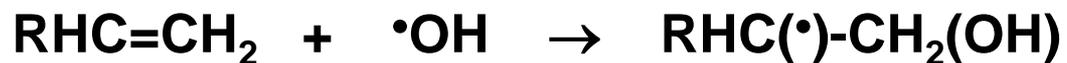
A alta reatividade do radical hidroxila justifica sua baixa concentração na atmosfera.

Áreas urbanas com muita vegetação apresentam altos níveis de aldeídos atmosféricos.

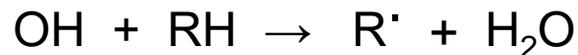
Hidrocarbonetos alifáticos reagem com radical hidroxila com perda de hidrogênio:



Hidrocarbonetos olefínicos (duplas ou triplas ligações) têm reações de adição com radical hidroxila:



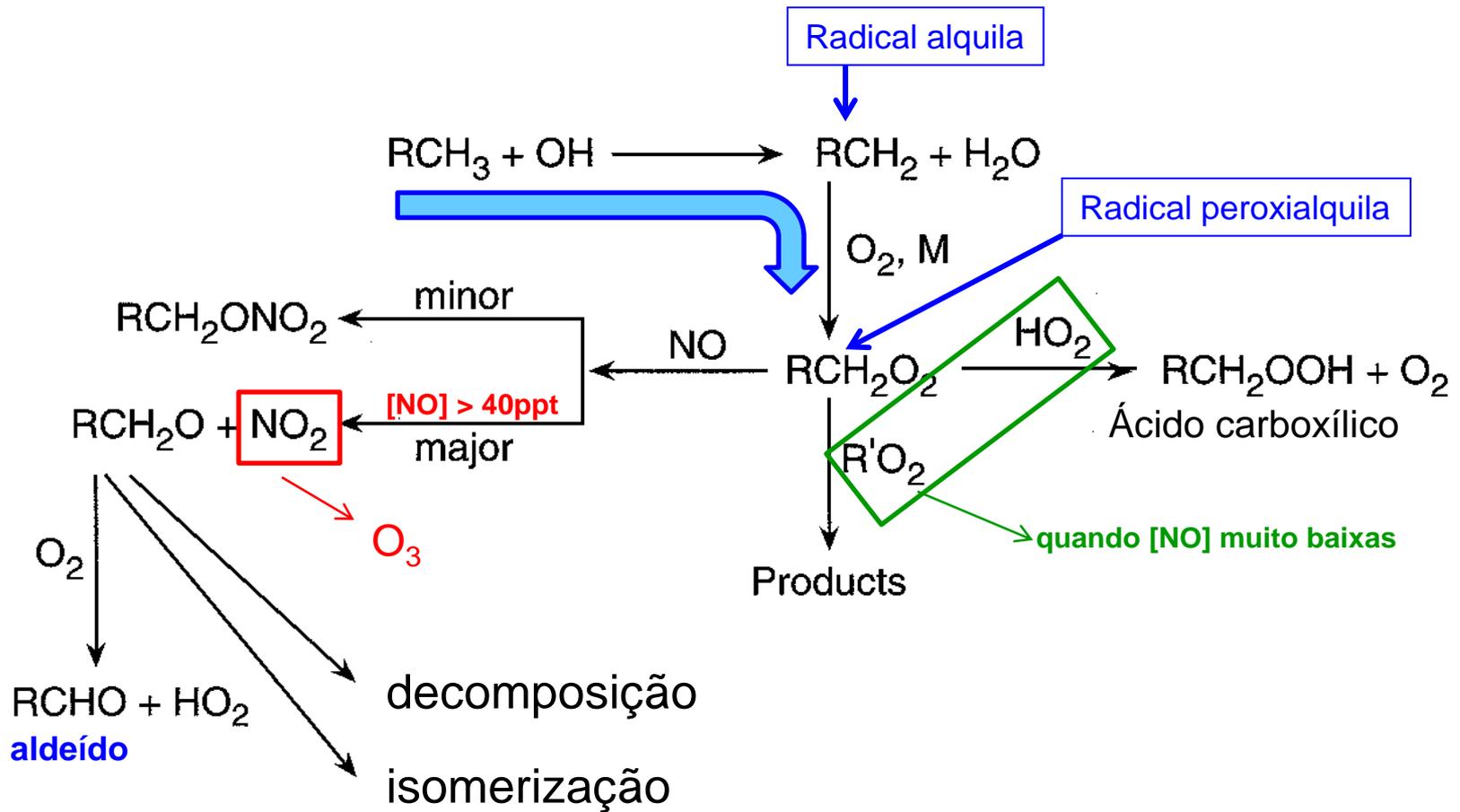
Constantes de velocidade (k) para reações de alcanos com radical OH



cadeia carbônica ↑ valor de k ↑

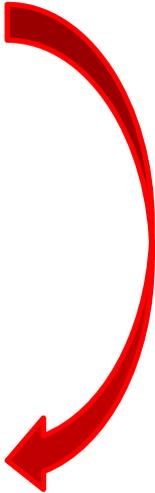
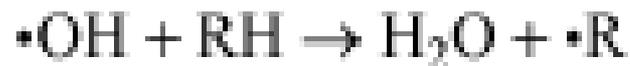
ramificação da cadeia ↑ valor de k ↑

| Alkane | k ($10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) at 298 K |
|---------------------------|--|
| Methane | 0.00618 |
| Ethane | 0.254 |
| Propane | 1.12 |
| <i>n</i> -Butane | 2.44 |
| 2-Methylpropane | 2.19 |
| <i>n</i> -Pentane | 4.0 |
| 2-Methylbutane | 3.7 |
| 2,2-Dimethylpropane | 0.85 |
| <i>n</i> -Hexane | 5.45 |
| 2-Methylpentane | 5.3 |
| 3-Methylpentane | 5.4 |
| 2,3-Dimethylbutane | 5.8 |
| <i>n</i> -Heptane | 7.0 |
| 2,2-Dimethylpentane | 3.4 |
| 2,2,3-Trimethylbutane | 4.2 |
| <i>n</i> -Octane | 8.7 |
| 2,2,4-Trimethylpentane | 3.6 |
| 2,2,3,3-Tetramethylbutane | 1.05 |
| <i>n</i> -Nonane | 10.0 |
| <i>n</i> -Decane | 11.2 |
| <i>n</i> -Undecane | 12.9 |
| <i>n</i> -Dodecane | 13.9 |
| <i>n</i> -Tridecane | 16 |
| <i>n</i> -Tetradecane | 18 |
| <i>n</i> -Pentadecane | 21 |
| <i>n</i> -Hexadecane | 23 |
| Cyclopropane | 0.084 |
| Cyclobutane | 1.5 |
| Cyclopentane | 5.02 (4.8) ^F |
| Cyclohexane | 7.21 (7.2) ^F |
| Cycloheptane | 13 |



Resumo da oxidação dos alcanos pelo radical OH no ar.

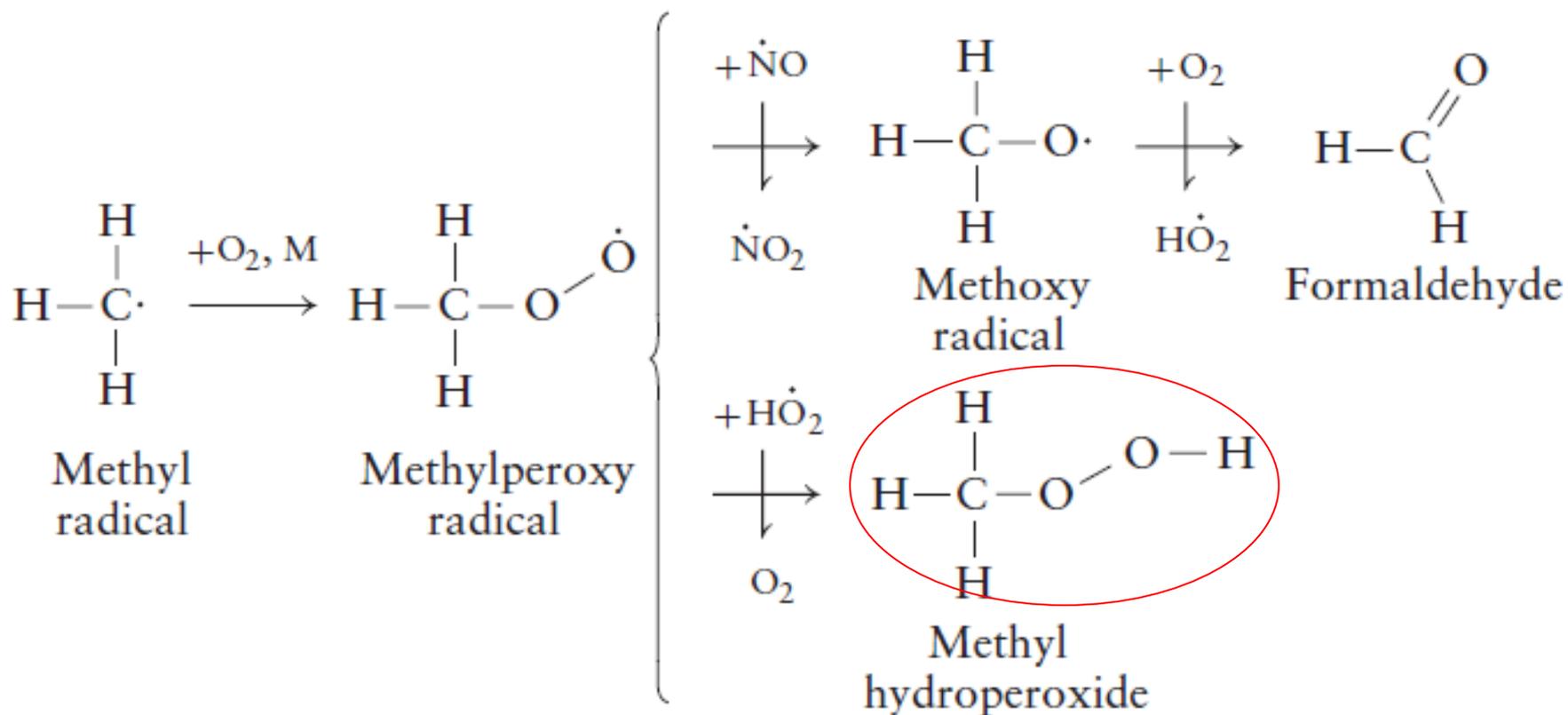
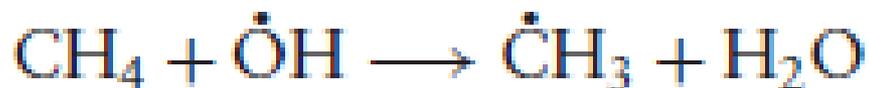
Resumo das reações de oxidação dos **alcanos** em presença de NO_x, produzindo ozônio

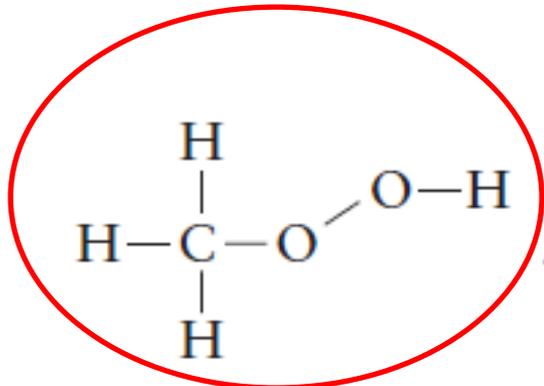


Alta concentração de NO_x,
aumenta produção de O₃

Alguns mecanismos de reação de oxidação de COVs

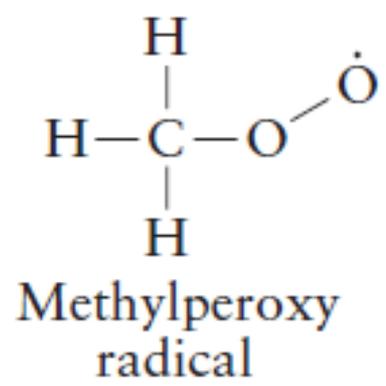
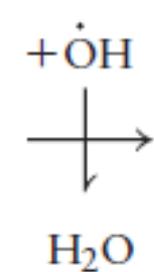
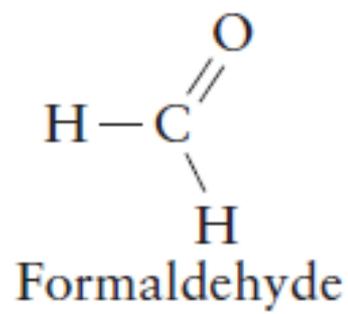
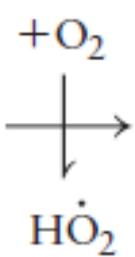
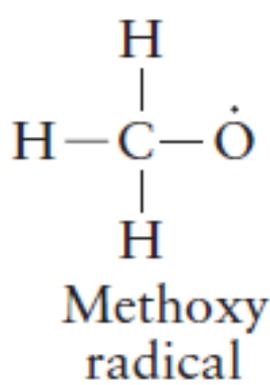
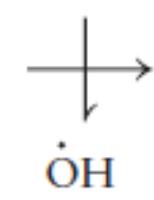
Oxidação do metano



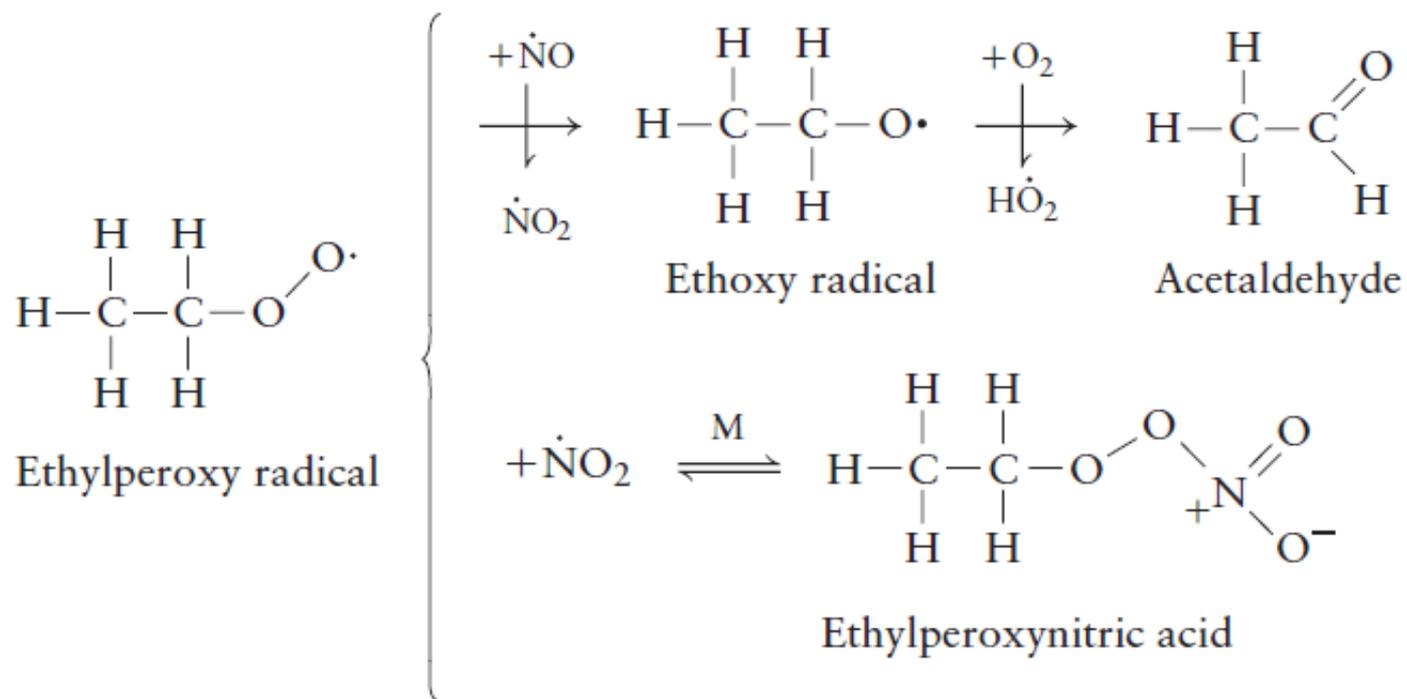
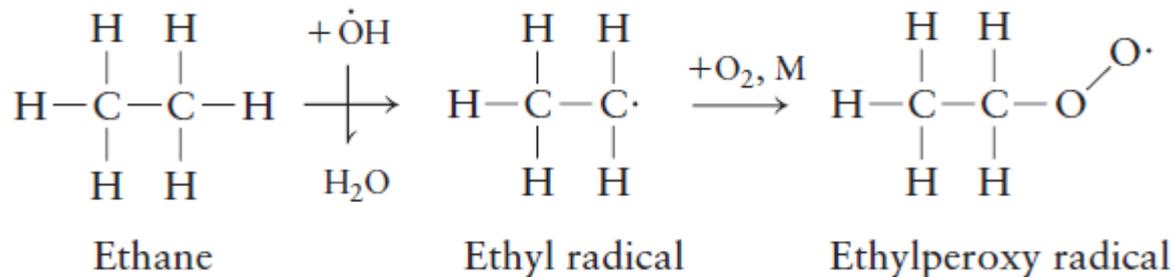


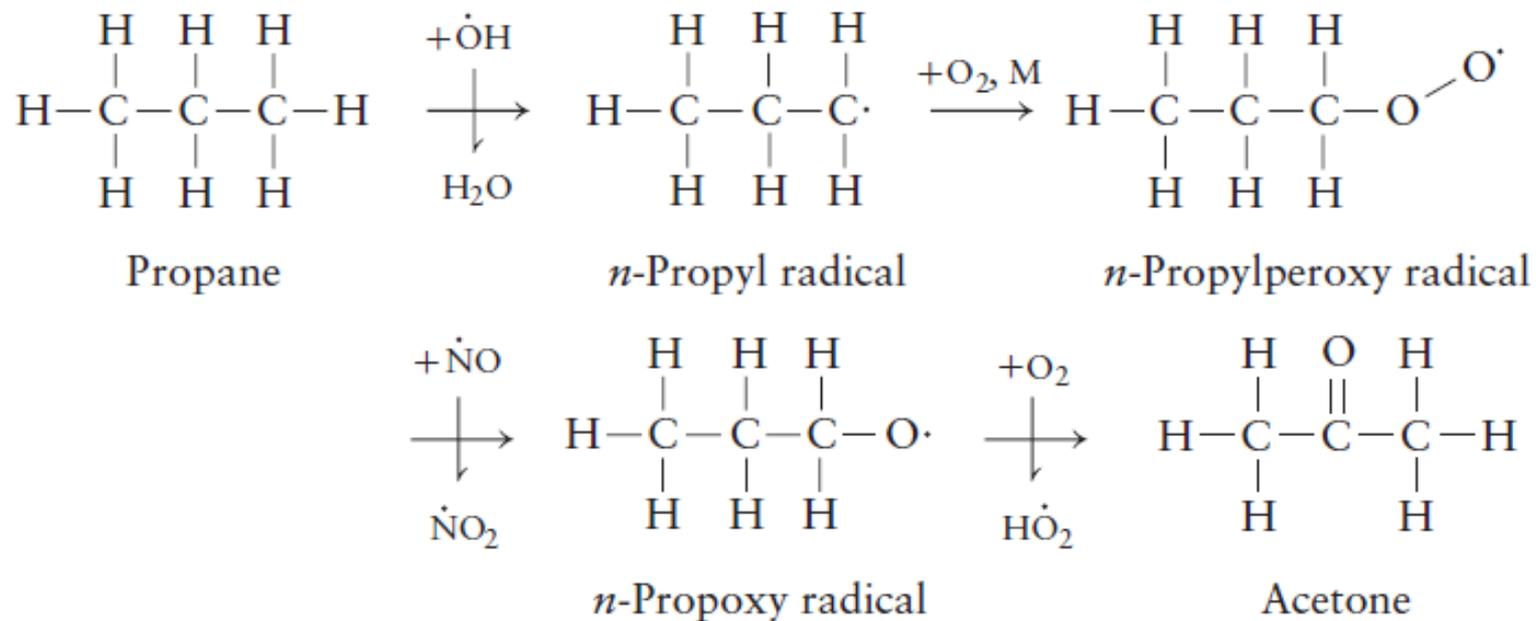
Methyl hydroperoxide

$+h\nu$
 $\lambda < 360 \text{ nm}$

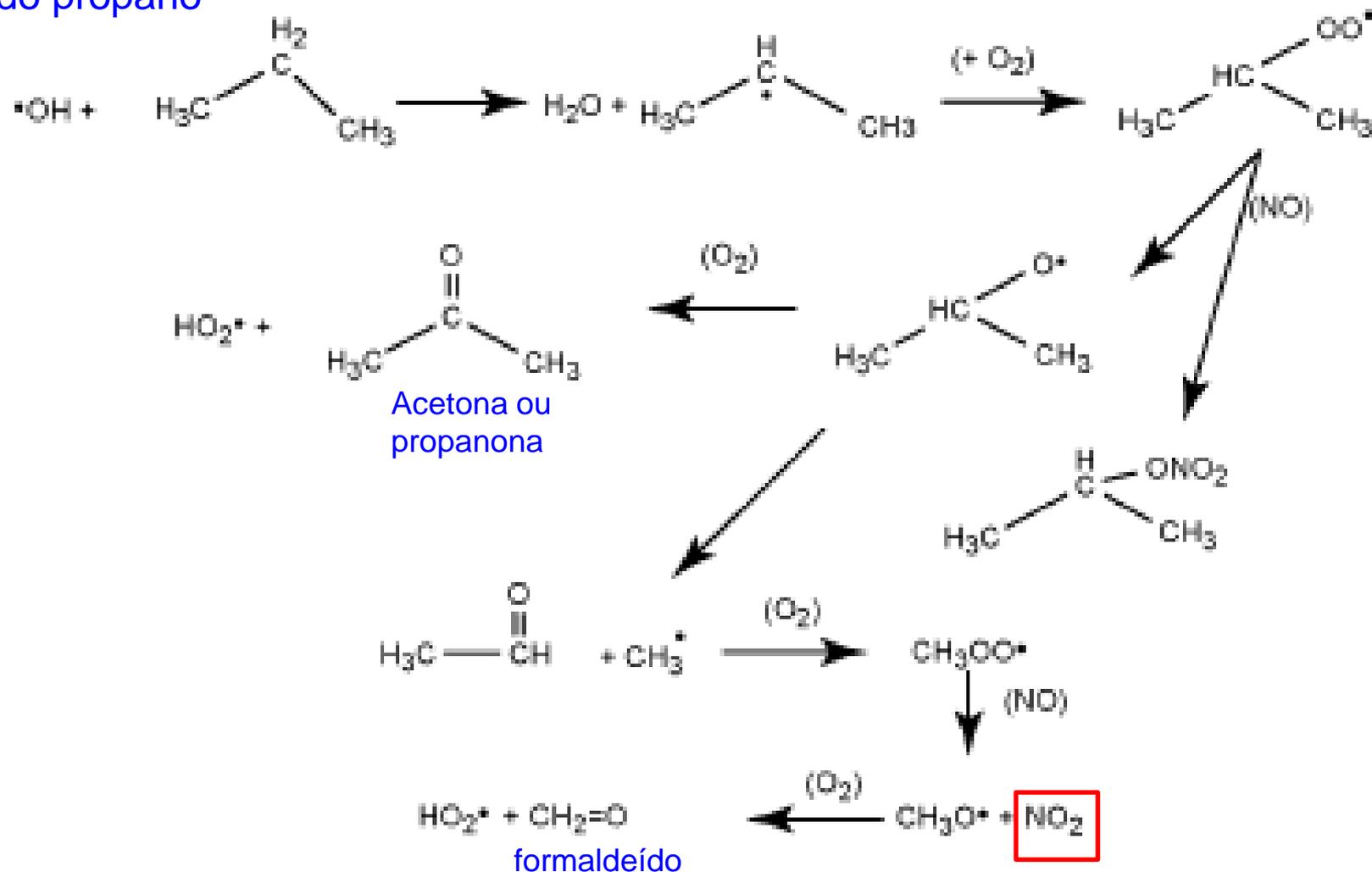


RO_2





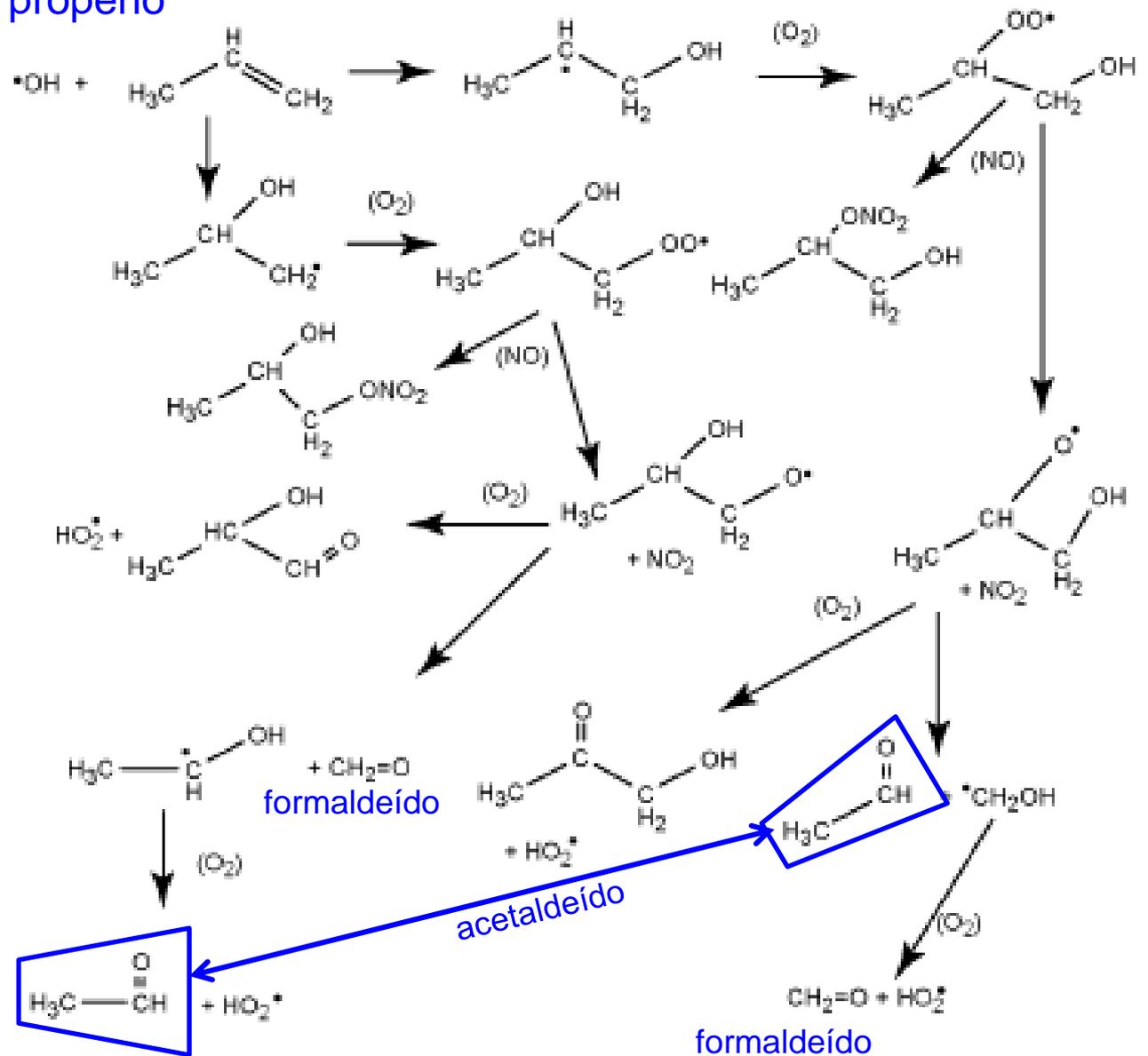
Mecanismo de reação do propano



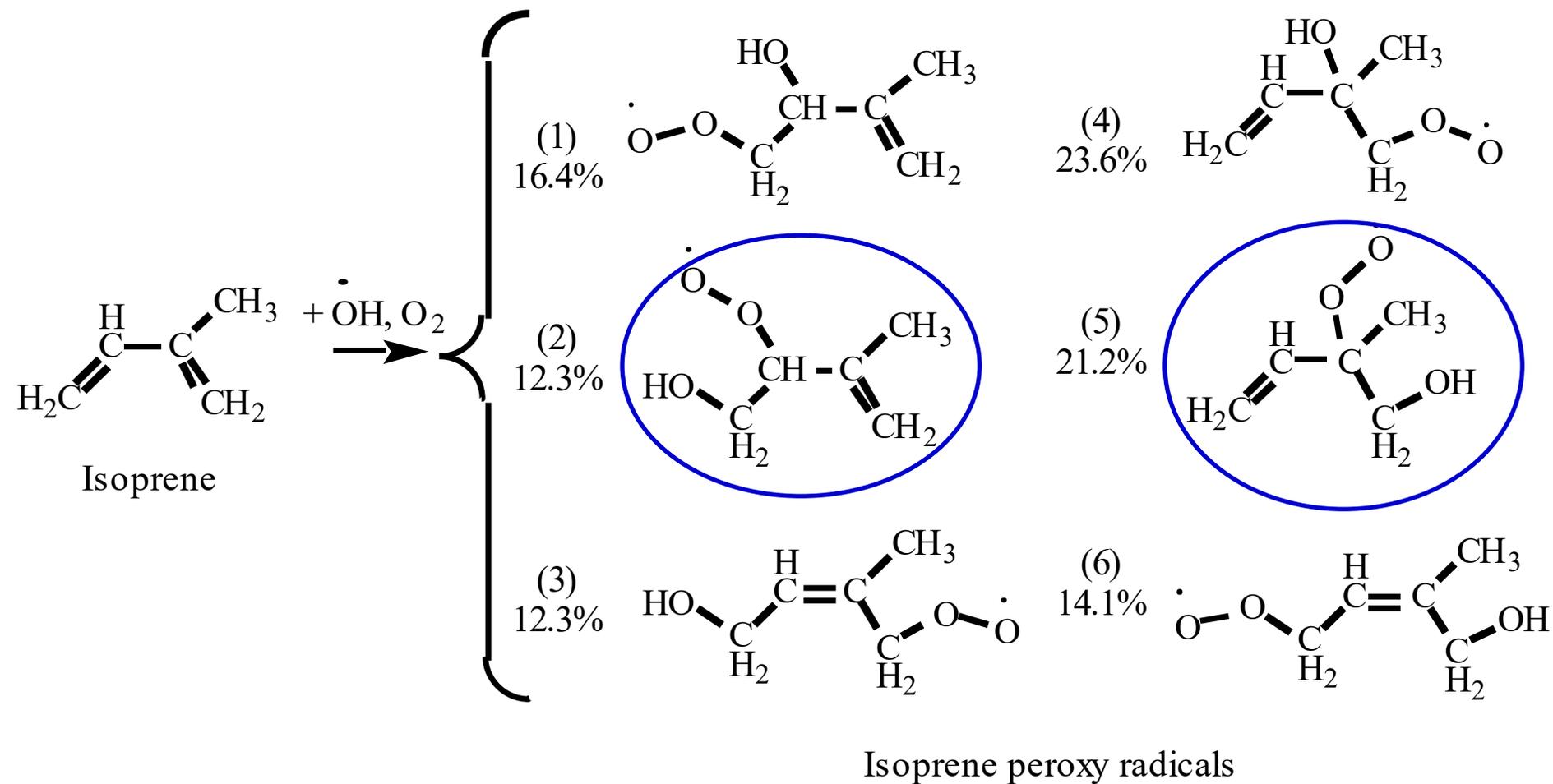
Obs: Carbonilas = cetonas + aldeídos

EPA, 2005

Mecanismo de reação do propeno



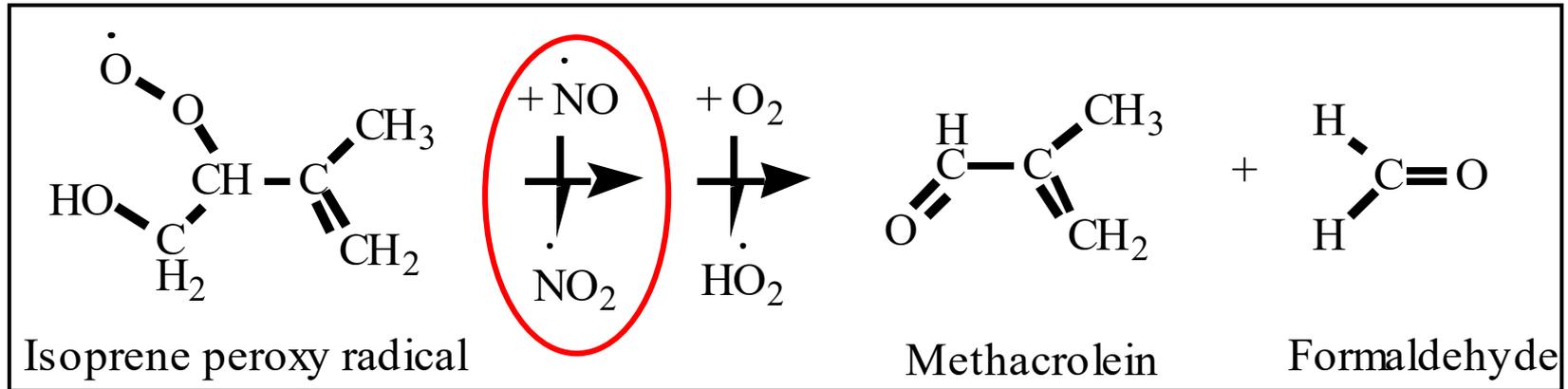
Reação do isopreno com OH



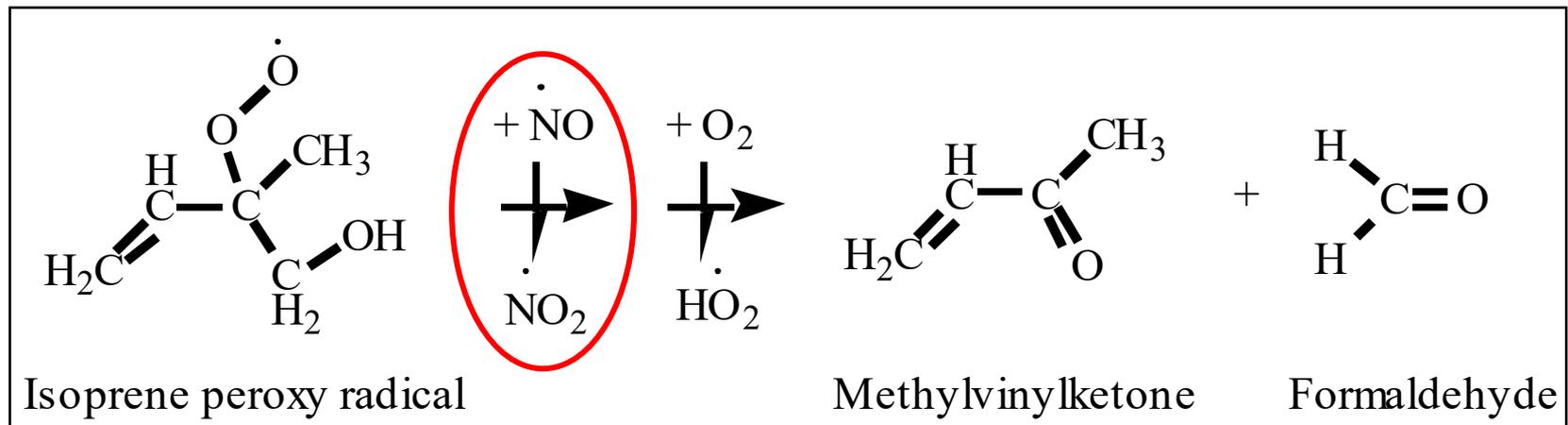
Todos estes seis produtos convertem NO para NO₂

Destino dos produtos de oxidação do isopreno

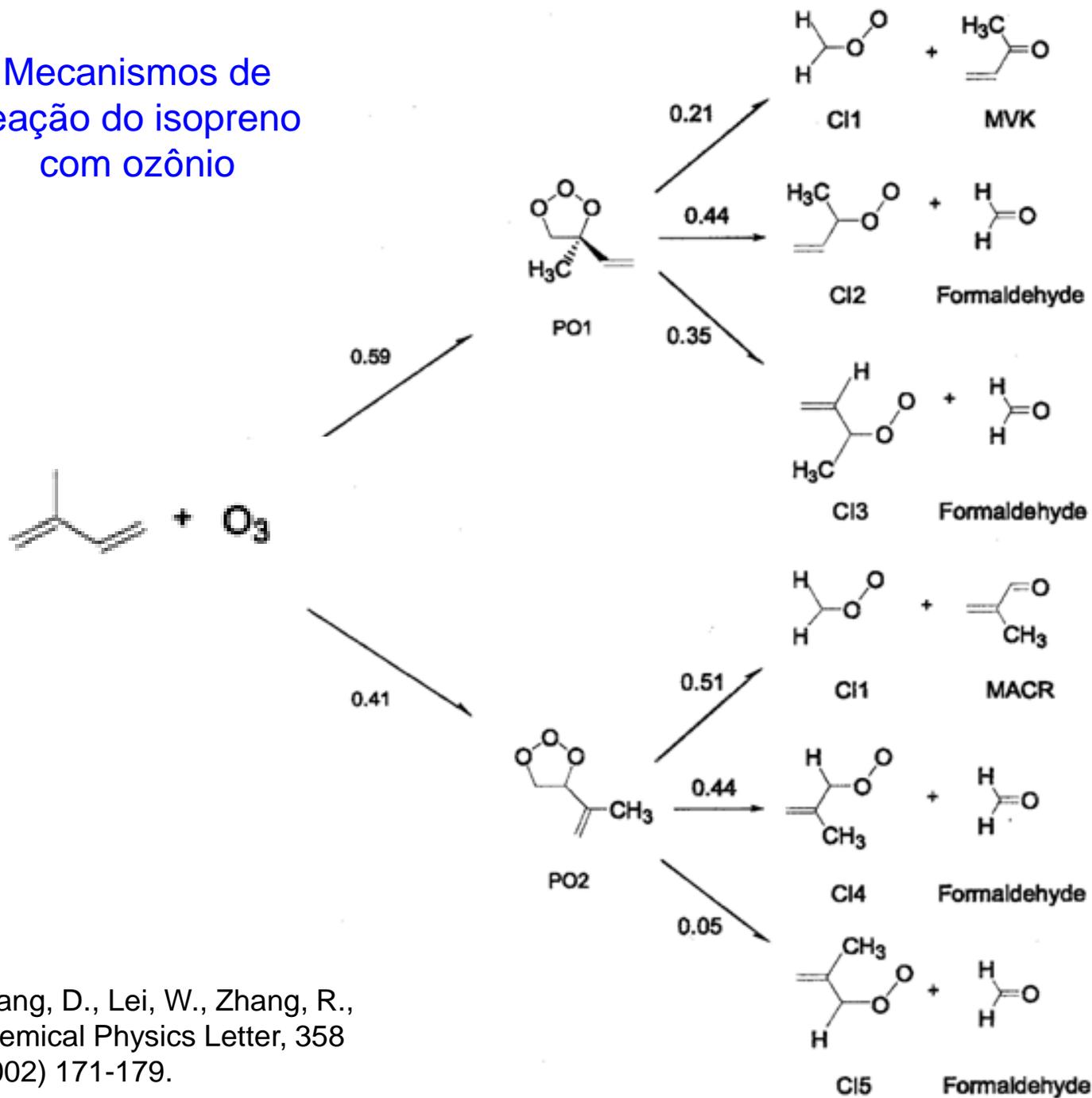
Produção de metacroleína via o segundo produto



Produção do metilvinilcetona via o quinto produto

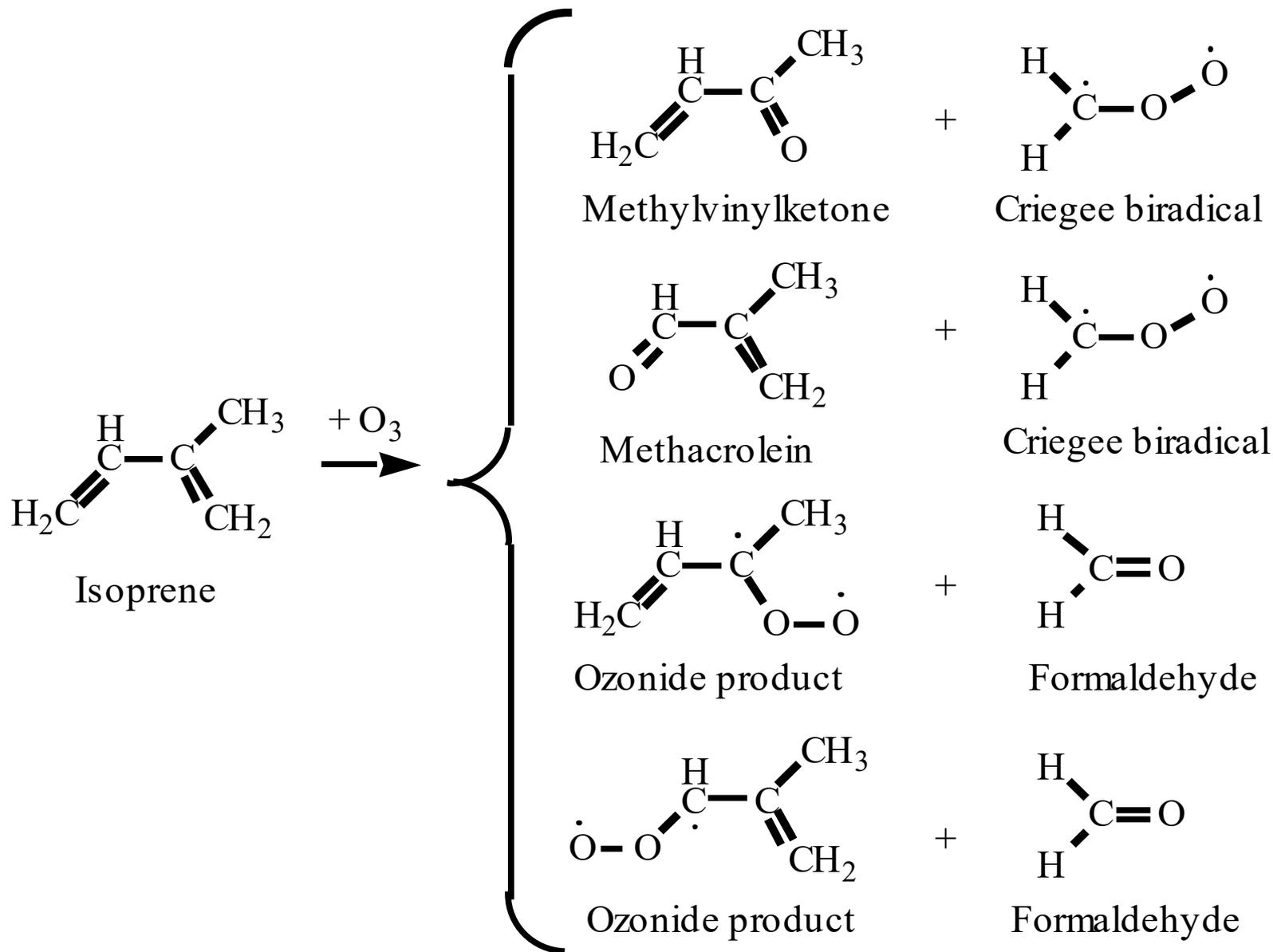


Mecanismos de reação do isopreno com ozônio



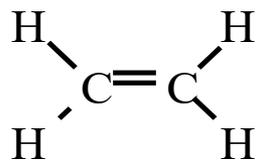
Zhang, D., Lei, W., Zhang, R.,
 Chemical Physics Letter, 358
 (2002) 171-179.

Reação do isopreno com ozônio

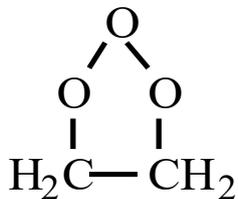


Reações de alceno com ozônio

Eteno

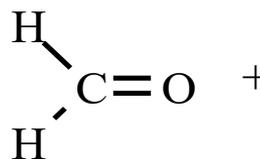


Ethene

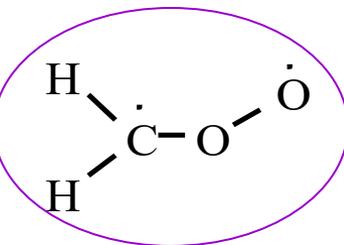


Ethene molozonide

37%

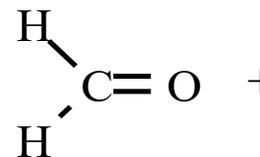


Formaldehyde

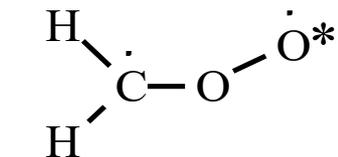


Criegee biradical

63%



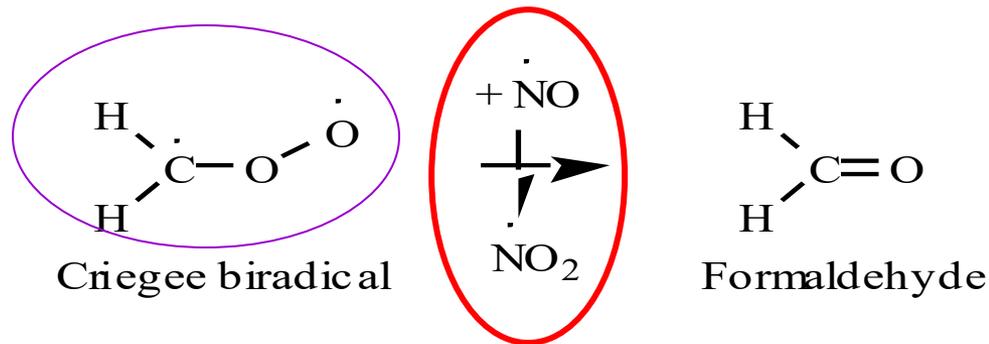
Formaldehyde



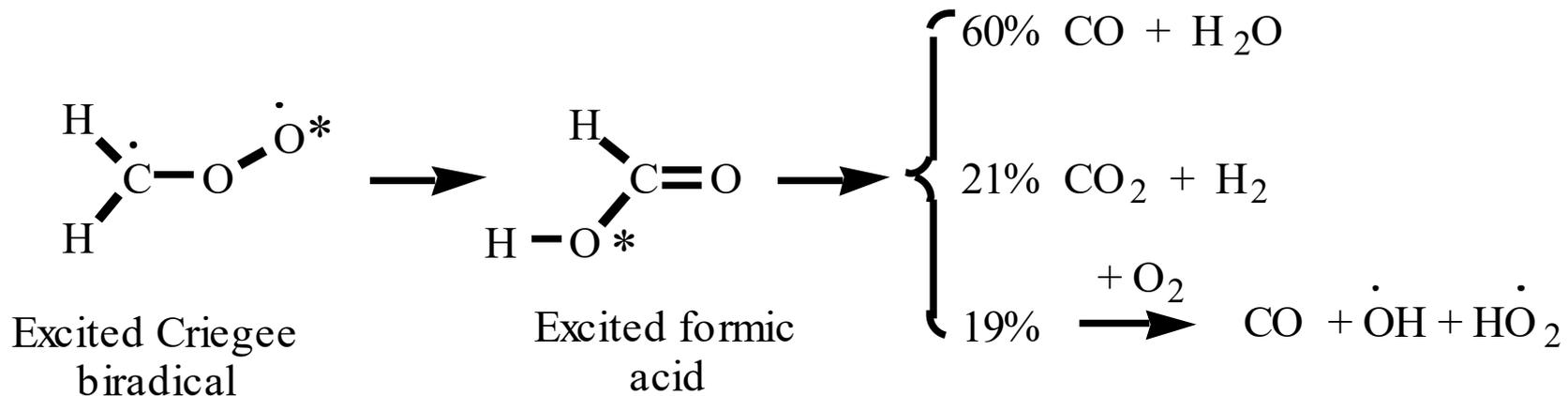
Excited Criegee biradical

Reações de alceno com ozônio

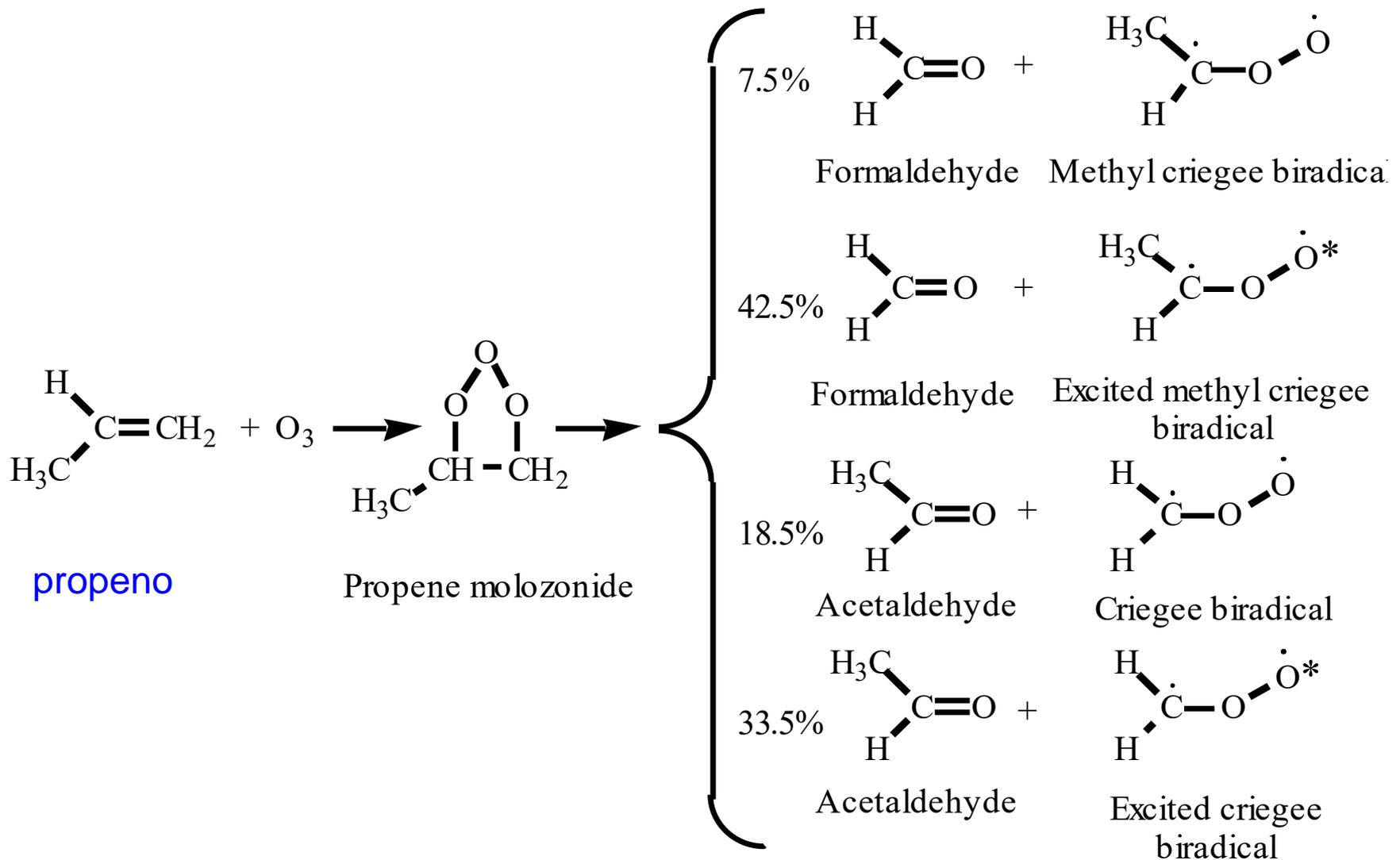
Reação do biradical Criegee com NO



Decomposição do biradical criegee excitado

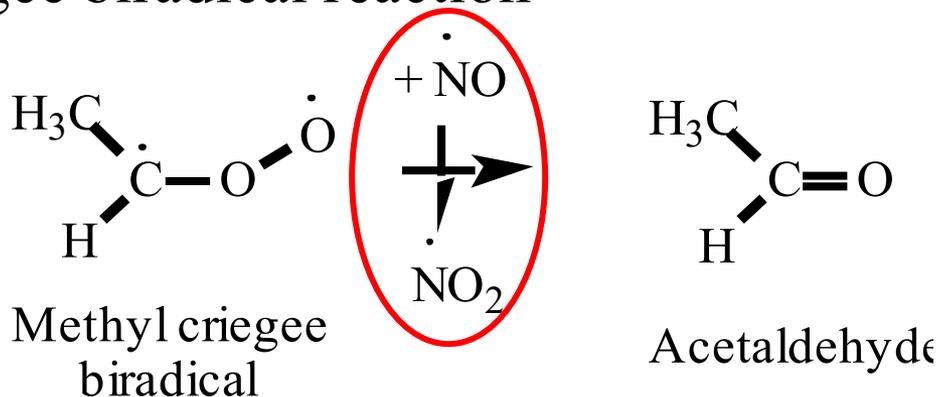


Reações de alceno com ozônio

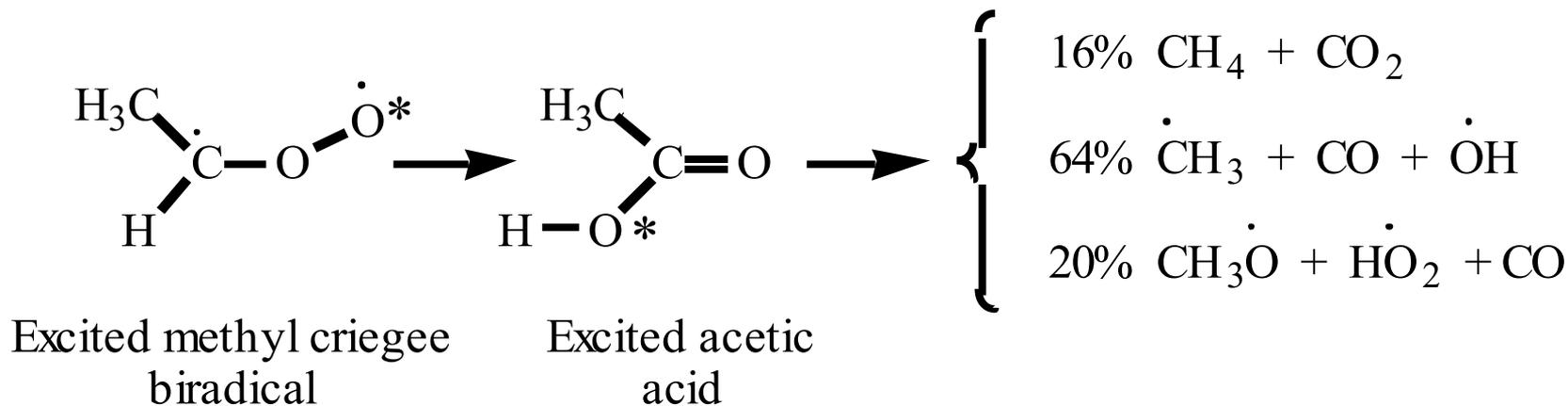


Reação de alceno com ozônio

Methylcriegee biradical reaction

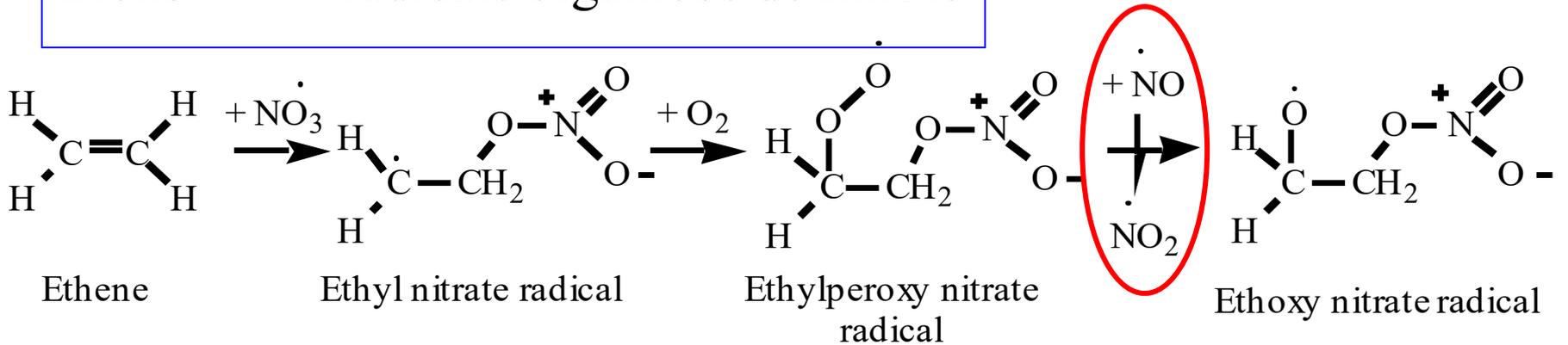


Excited methylcriegee biradical decomposition

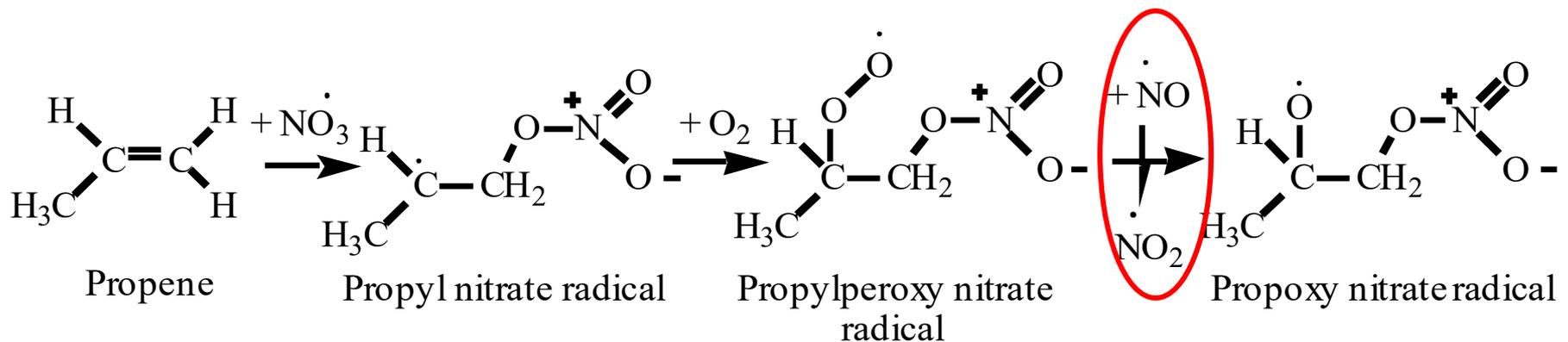


Reações de alceno com radical nitrato (NO_3)

Eteno \rightarrow radicais orgânicos de nitrato

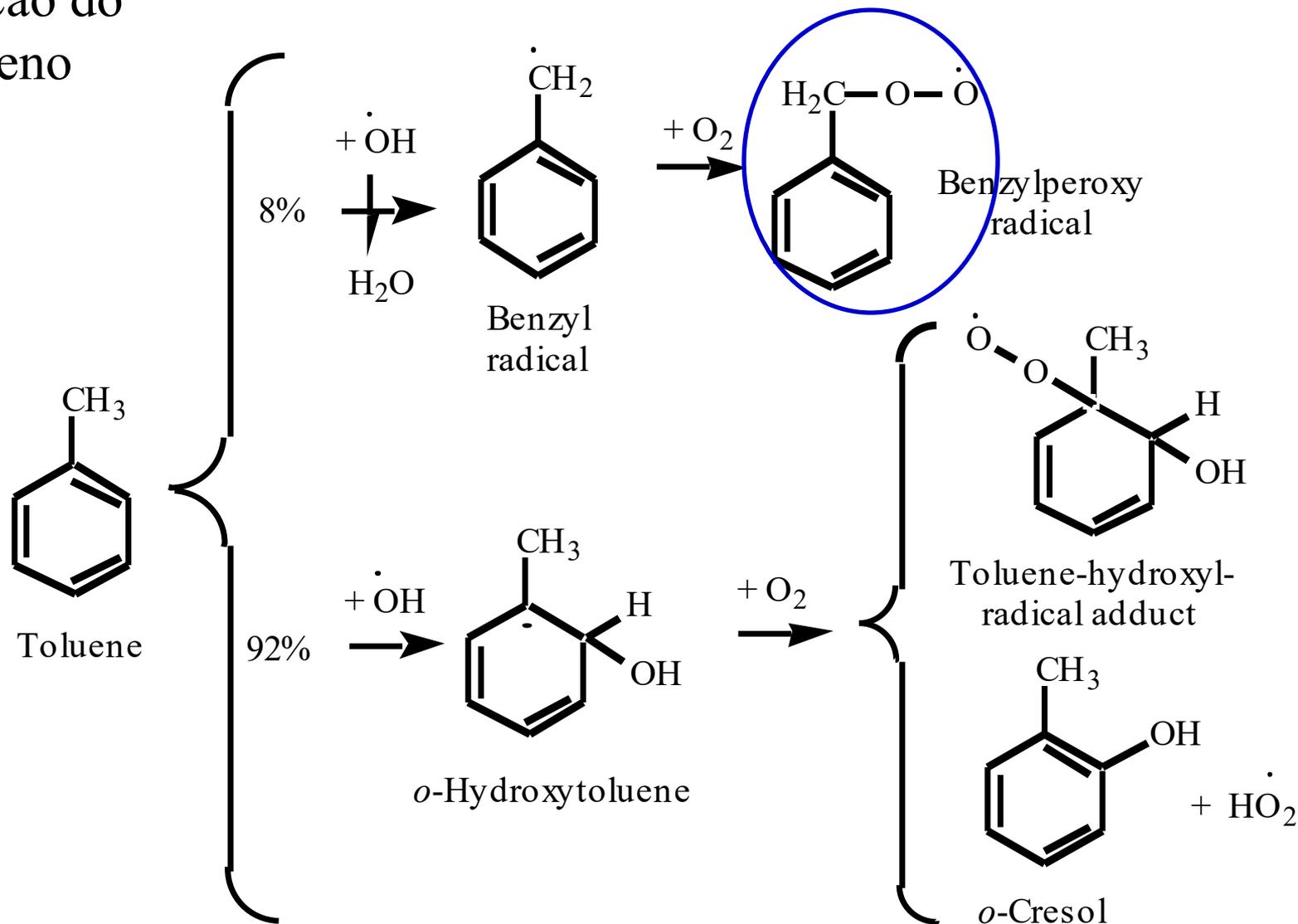


Propeno \rightarrow radicais orgânicos de nitrato



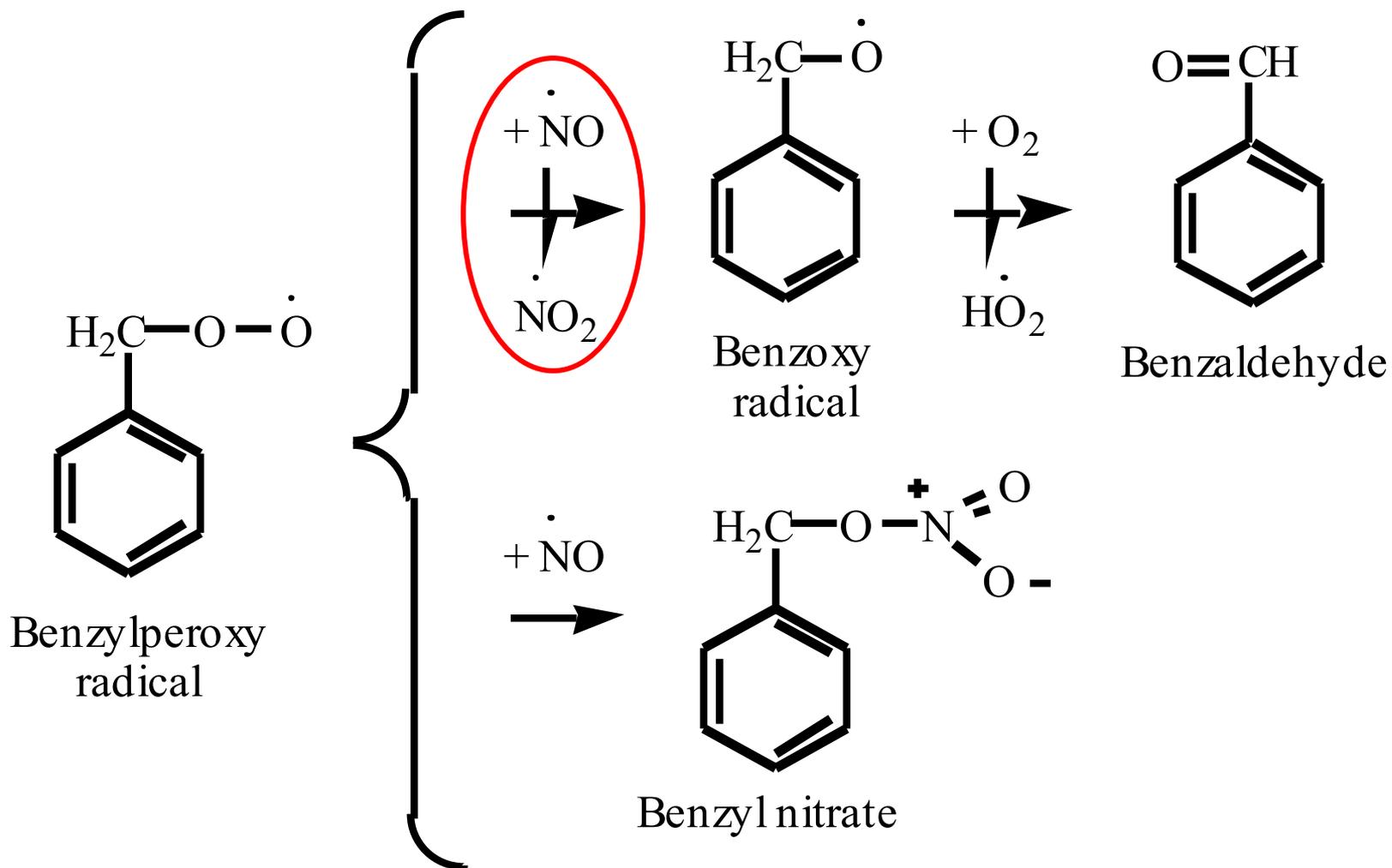
Reação dos compostos aromáticos com radical OH

Oxidação do tolueno



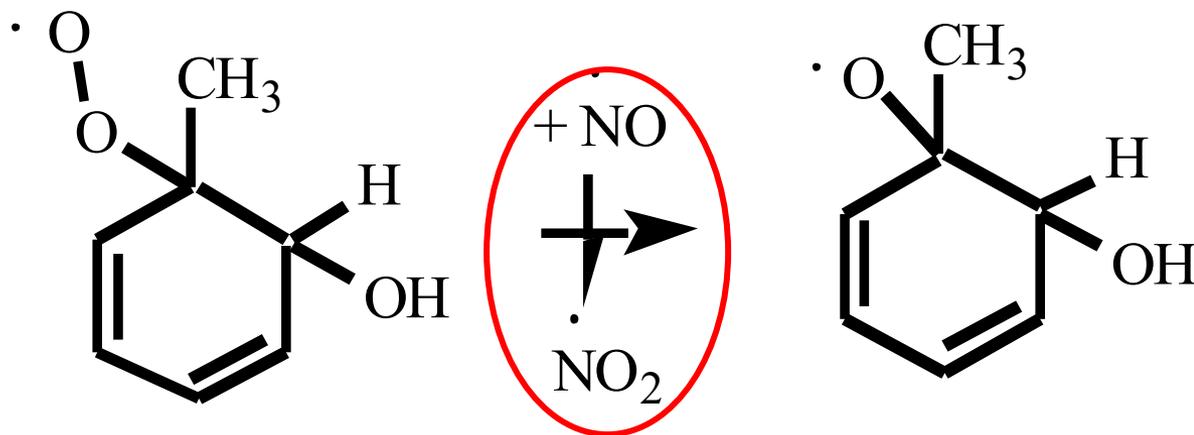
Reação dos compostos aromáticos com radical OH

Reação do benzilperoxi radical com NO



Reação dos compostos aromáticos com radical OH

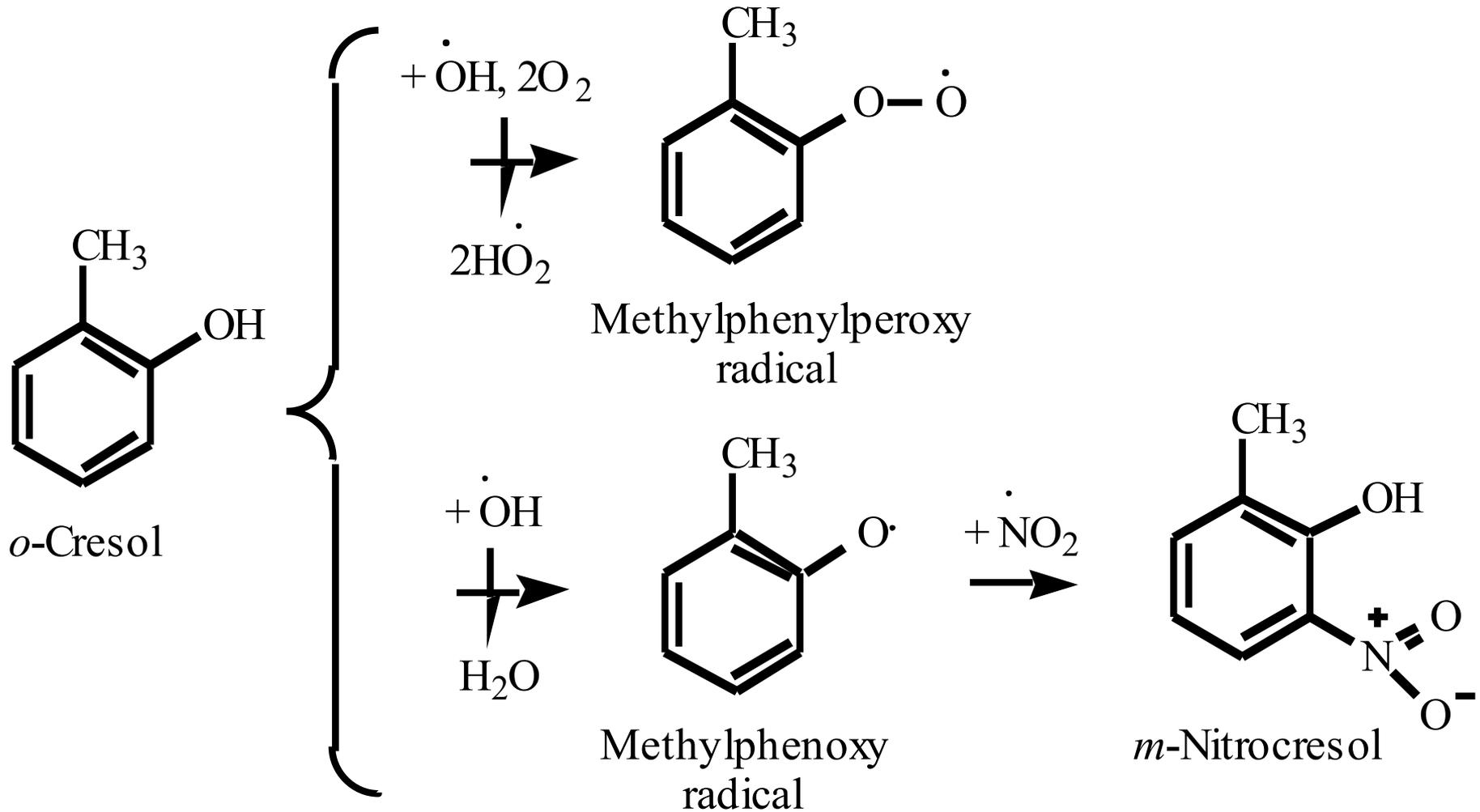
Reação do aducto tolueno-hidroxil radical



Toluene-hydroxyl
radical adduct

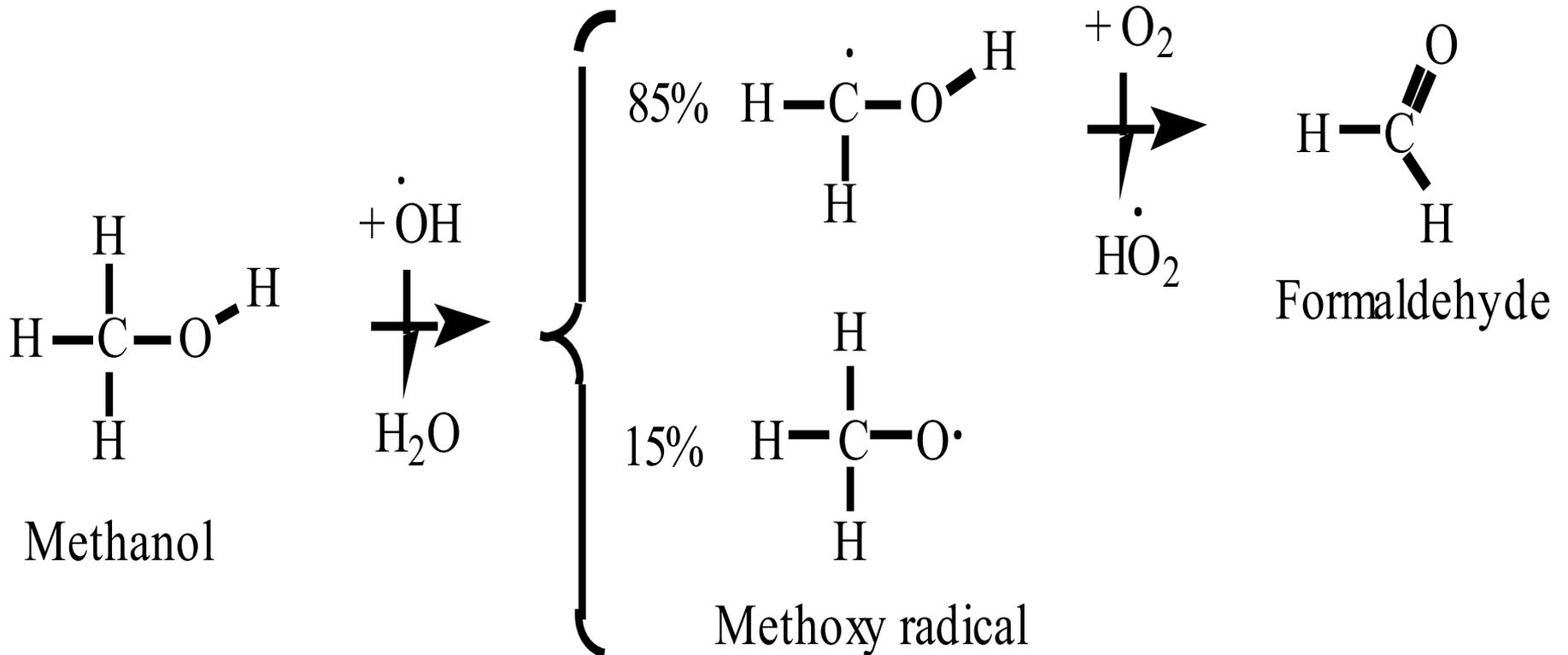
Destino do cresol

Cresol \rightarrow metilfenilperoxi radical e nitrocresol



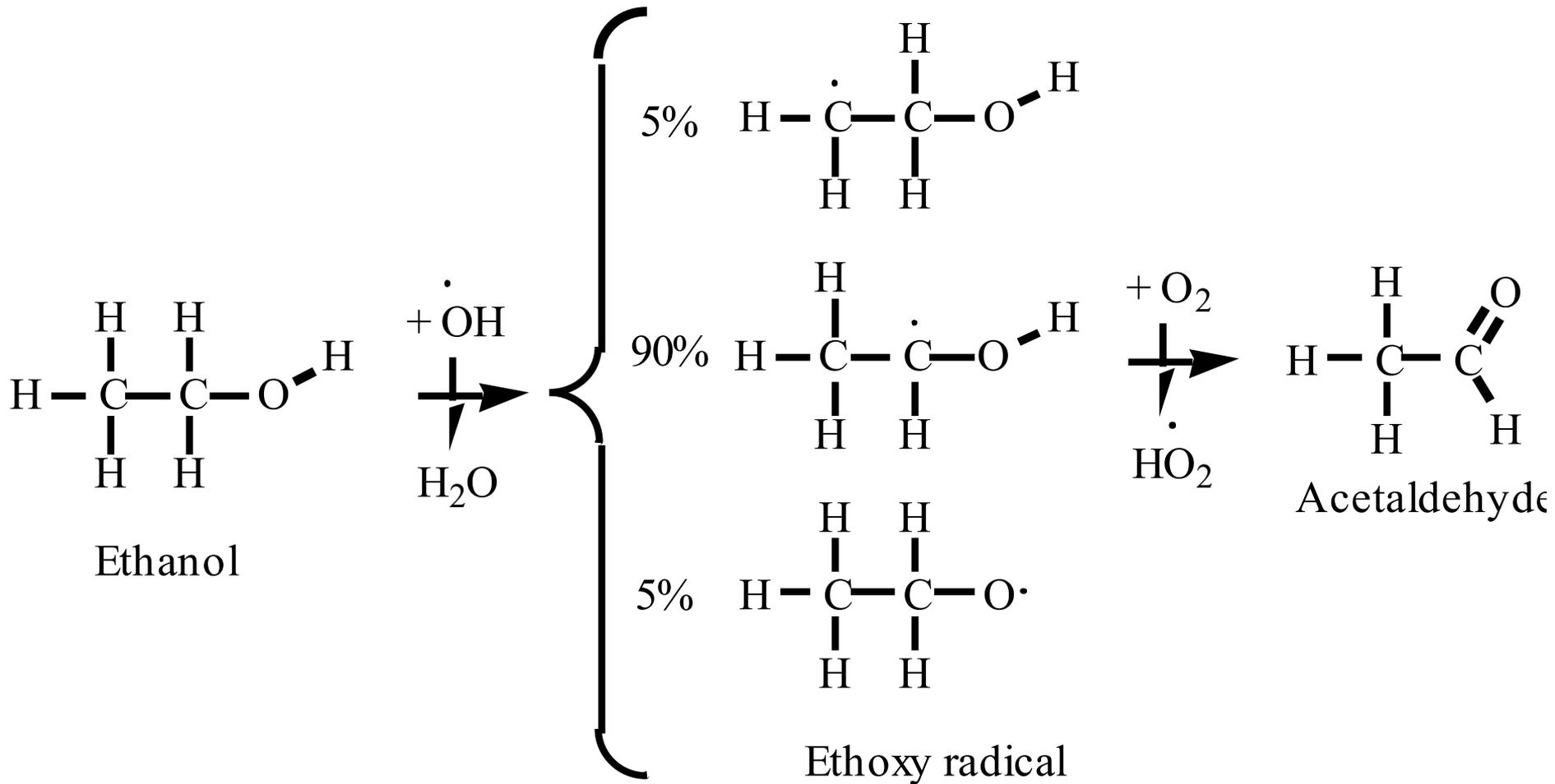
Reações dos alcóois

Oxidação do metanol por OH (36-h de tempo de vida)



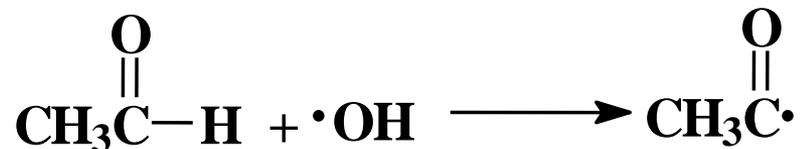
Reações dos alcóois

Oxidação do etanol por OH (10-h de tempo de vida)



Aldeídos podem sofrer mais reações formando PAN

Outro importante poluente atmosférico é o peroxiacilnitrato (PAN), formado a partir de compostos orgânicos no ar:



Entre os principais produtos do *smog* estão ozônio e PAN (peroxiacetilnitrato). O **PAN**, como o ozônio, é um composto tóxico potente e é formado a partir dos hidrocarbonetos na atmosfera.

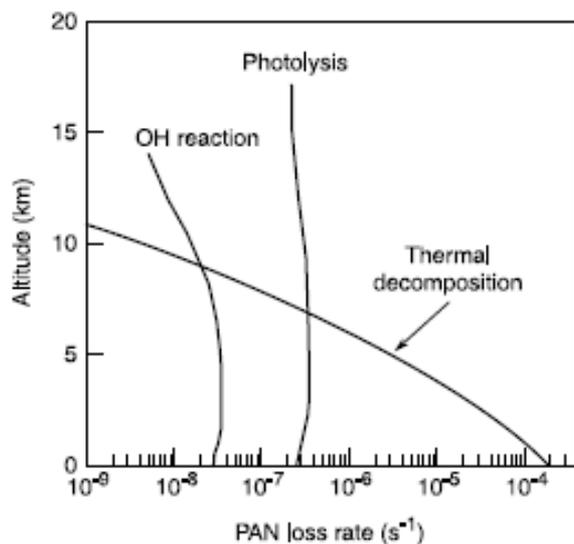
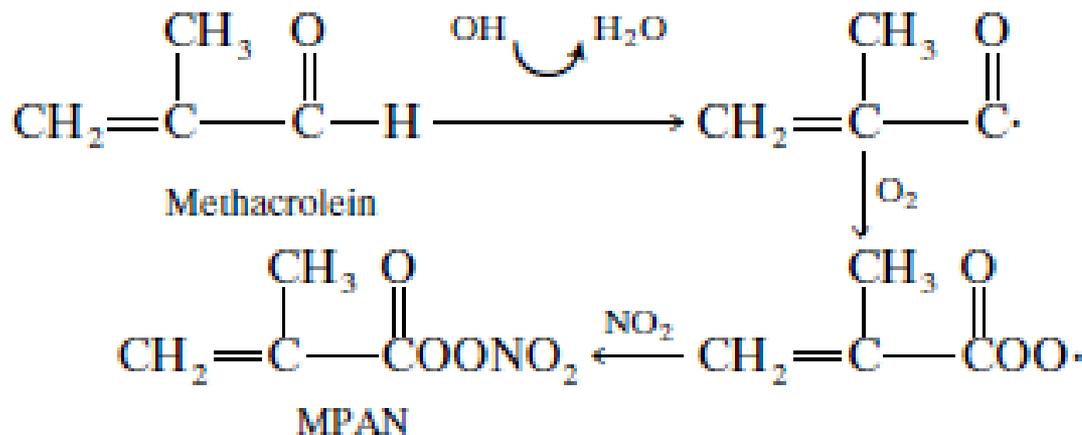
A mistura dos gases O₃, PAN e NO₂ produzem a aparência castanha e/ou enfumaçada no ar.

Estruturas e nomes de alguns peroxiacil nitratos encontrados na atmosfera ou estudos de laboratório

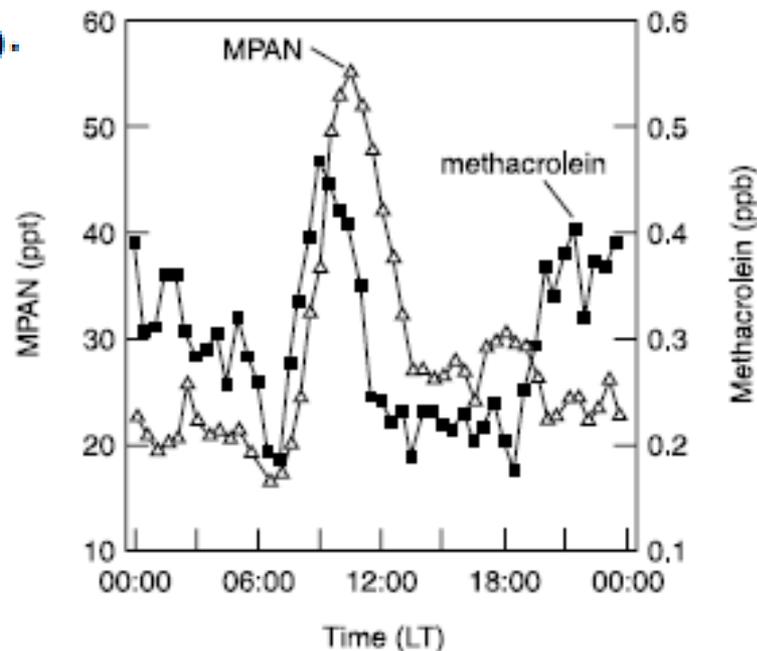
| Name | Acronym | Structure |
|--|---------|--|
| Peroxyacetyl nitrate (peroxyacetic nitric anhydride) | PAN | $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{COONO}_2 \end{array}$ |
| Peroxypropionyl nitrate | PPN | $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{COONO}_2 \end{array}$ |
| Peroxy- <i>n</i> -butyryl nitrate | PnBN | $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{COONO}_2 \end{array}$ |
| Peroxybenzoyl nitrate | PBzN | $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_6\text{H}_5\text{COONO}_2 \end{array}$ |
| Peroxymethacryloyl nitrate | MPAN | $\begin{array}{c} \text{H}_3\text{C} \quad \text{O} \\ \quad \parallel \\ \text{CH}_2=\text{C}-\text{COONO}_2 \end{array}$ |

- em geral, PAN >> PPN e outros
- Regiões altamente poluídas PAN ~70 ppb
- tempo de vida destes compostos entre 30 e 100 minutos, devido decomposição térmica ⇒ reservatório de NO₂ durante a noite

Metacroleína (aldeído produto da oxidação do isopreno)



Velocidades de primeira ordem calculadas para perda de PAN

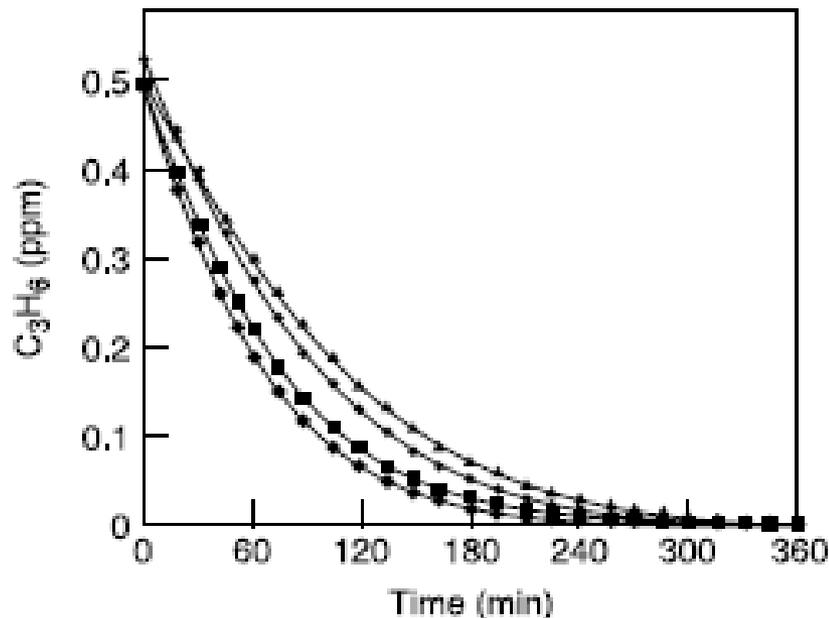


Variações diurnas das razões de mistura de MPAN e seu precursor metacroleína (região rural de Nashville)

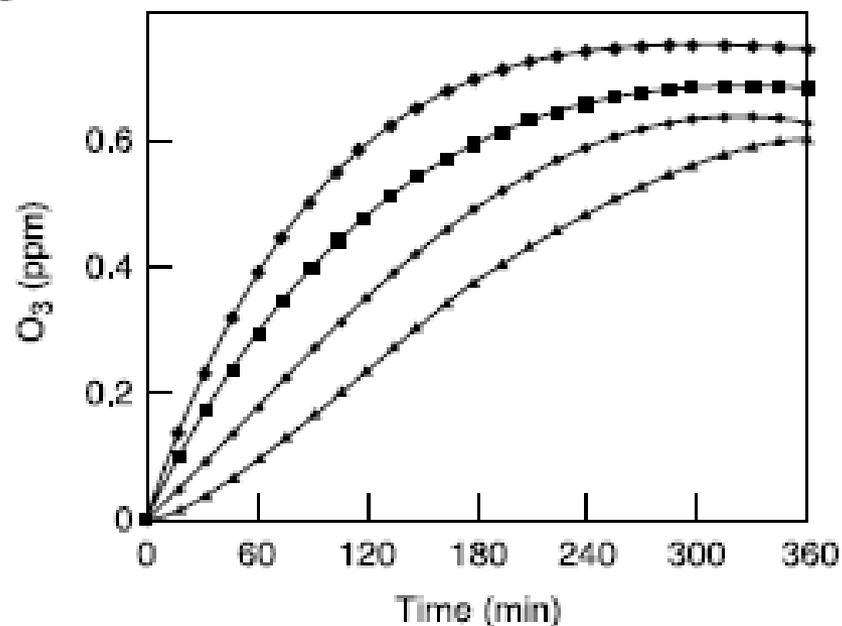
Efeito de presença inicial de PAN na produção de ozônio:

a) Variação de propeno consumido; b) variação de ozônio produzido

a)



b)



Temperature $\sim 30^\circ C$, relative humidity $\sim 60\%$, $[NO] = [NO_2] = 0.26$ ppm, $[C_3H_6] = 0.5$ ppm. (▲) No added PAN; (●) 0.06 ppm PAN added; (■) 0.13 ppm PAN added; (◆) 0.26 ppm added PAN (adapted from Carter *et al.*, 1981a).

Escalas de reatividade – conceito baseado na classificação dos COVs em termos do potencial para produção de ozônio.

Pode ser baseado em diferentes parâmetros: velocidades de reação, rendimento dos produtos e efeitos observados a partir da mistura VOC/NOx em presença de radiação.

Reações do radical OH

⇒ fato: responsável por processos que “consomem” a maioria dos hidrocarbonetos, produzindo mais radicais livres (HO_2 , RO_2) que oxidam NO para NO_2 , causando mais formação de O_3 .

Escalas de reatividade dos hidrocarbonetos com OH

| Class | k_{OH}^a (298 K) | $\tau_{1/2}^{OH}^b$ | Typical hydrocarbons |
|-------|--------------------------|---------------------|--|
| I | $\leq 8 \times 10^{-14}$ | ≥ 100 days | CH ₄ |
| II | $(8-80) \times 10^{-14}$ | 10-100 days | Acetylene, ethane, benzene |
| III | $(8-80) \times 10^{-13}$ | 1-10 days | Ethene, propane, toluene |
| IV | $(8-80) \times 10^{-12}$ | 2-24 h | Propene, <i>o</i> -, <i>m</i> -, and <i>p</i> -xylene, 1,2,4- and 1,2,5-trimethylbenzene |
| V | $\geq 8 \times 10^{-11}$ | <2 h | 2-Methyl-2-butene, <i>d</i> -limonene |

Source: Adapted from Darnall *et al.* (1976).

^a Units of cm³ molecule⁻¹ s⁻¹; note that k (OH + CH₄) has been revised downward (Chapter 6).

^b Half-lives in atmosphere with respect to reaction with OH assuming [OH] = 1.5×10^6 radicals cm⁻³.

TABLE 16.8 Typical Calculated Incremental Reactivities and Maximum Ozone as a Function of the VOC/NO₂ Ratio^a

| VOC/NO ₂ ratio | 4 | 6 | 8 | 10 | 12 | 16 | 20 | 40 |
|---|--|-------|-------|-------|--------|--------|--------|--------|
| Base case max O ₃ (ppb) ^b | 72 | 160 | 214 | 215 | 209 | 194 | 180 | 139 |
| Molecule (k ^{cm}) ^c | Incremental reactivity (Molecules of O ₃ /C atoms of VOC added) | | | | | | | |
| CO (2.4 × 10 ⁻¹²) ^c | 0.011 | 0.025 | 0.022 | 0.018 | 0.016 | 0.012 | 0.010 | 0.005 |
| Ethane (2.5 × 10 ⁻¹²) | 0.024 | 0.054 | 0.041 | 0.031 | 0.026 | 0.018 | 0.015 | 0.007 |
| <i>n</i> -Butane (2.4 × 10 ⁻¹²) | 0.10 | 0.22 | 0.16 | 0.12 | 0.098 | 0.069 | 0.052 | 0.019 |
| Ethene (8.5 × 10 ⁻¹²) | 0.85 | 1.65 | 0.90 | 0.64 | 0.50 | 0.33 | 0.30 | 0.14 |
| Propene (2.6 × 10 ⁻¹¹) | 1.28 | 2.04 | 1.03 | 0.61 | 0.51 | 0.39 | 0.25 | 0.14 |
| <i>trans</i> -2-Butene (6.4 × 10 ⁻¹¹) | 1.42 | 2.02 | 0.97 | 0.62 | 0.48 | 0.31 | 0.23 | 0.054 |
| Benzene (1.2 × 10 ⁻¹²) | 0.038 | 0.082 | 0.033 | 0.011 | 0.003 | -0.002 | -0.004 | -0.002 |
| Toluene (6.0 × 10 ⁻¹²) | 0.26 | 0.52 | 0.16 | 0.04 | -0.021 | -0.036 | -0.058 | -0.051 |
| Formaldehyde (9.2 × 10 ⁻¹²) | 2.42 | 3.28 | 1.20 | 0.77 | 0.48 | 0.32 | 0.24 | 0.051 |
| Acetaldehyde (1.6 × 10 ⁻¹¹) | 1.34 | 1.83 | 0.83 | 0.55 | 0.42 | 0.29 | 0.24 | 0.098 |
| Benzaldehyde (1.3 × 10 ⁻¹¹) | -0.11 | -0.15 | -0.27 | -0.34 | -0.37 | -0.41 | -0.41 | -0.40 |
| Methanol (9.3 × 10 ⁻¹²) | 0.12 | 0.27 | 0.17 | 0.12 | 0.091 | 0.066 | 0.055 | 0.029 |
| Ethanol (3.2 × 10 ⁻¹²) | 0.18 | 0.37 | 0.22 | 0.14 | 0.10 | 0.065 | 0.038 | 0.006 |

^a From Carter and Atkinson (1989) calculated using the EKMA model with low dilution and an eight-component surrogate mixture of organics chosen to be representative of emissions into California's South Coast air basin. Note that the absolute values used may have changed for some components since the original publication due to further refinement of the model.

^b Peak ozone predicted from photolysis of initial base case mixture with the specified VOC/NO₂ ratio.

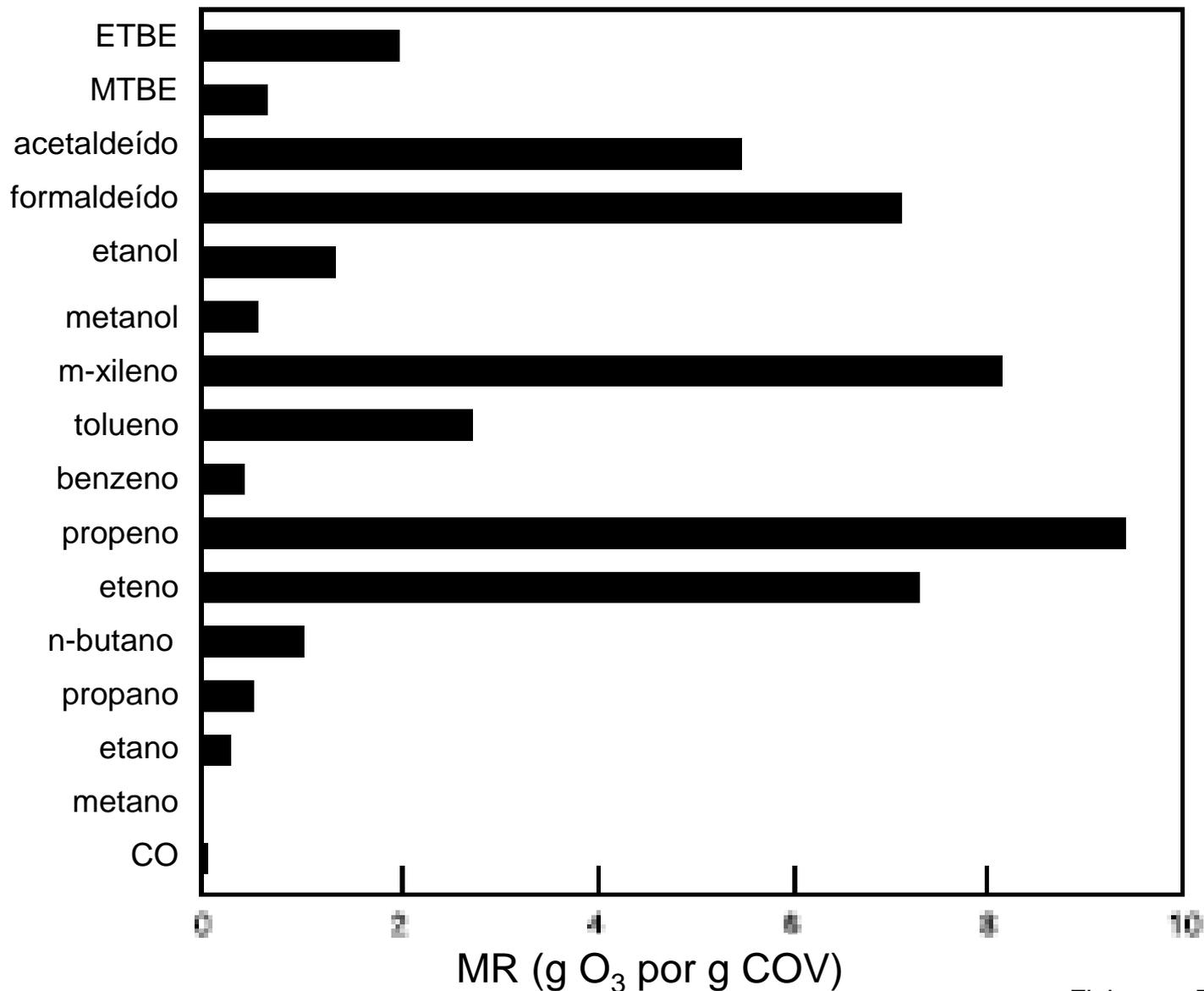
^c Rate constants for reaction with OH at 298 K in units of cm² molecule⁻¹ s⁻¹ taken from Atkinson (1989, 1994) and Atkinson *et al.* (1997a, 1997b).

TABLE 16.9 Maximum Incremental Reactivities (MIR)
for Some VOCs

| VOC | MIR ^a (grams of O ₃ formed per gram of VOC added) |
|-----------------------------------|---|
| Carbon monoxide | 0.054 |
| Methane | 0.015 |
| Ethane | 0.25 |
| Propane | 0.48 |
| n-Butane | 1.02 |
| Ethene | 7.4 |
| Propene | 9.4 |
| 1-Butene | 8.9 |
| 2-Methylpropene (isobutene) | 5.3 |
| 1,3-Butadiene | 10.9 |
| 2-Methyl-1,3-butadiene (isoprene) | 9.1 |
| α-Pinene | 3.3 |
| β-Pinene | 4.4 |
| Ethyne (acetylene) | 0.50 |
| Benzene | 0.42 |
| Toluene | 2.7 |
| m-Xylene | 8.2 |
| 1,3,5-Trimethylbenzene | 10.1 |
| Methanol | 0.56 |
| Ethanol | 1.34 |
| Formaldehyde | 7.2 |
| Acetaldehyde | 5.5 |
| Benzaldehyde | -0.57 |
| Methyl <i>tert</i> -butyl ether | 0.62 |
| Ethyl <i>tert</i> -butyl ether | 2.0 |
| Acetone | 0.56 |
| C ₄ ketones | 1.18 |
| Methyl nitrite | 9.5 |

^a From Carter (1994).

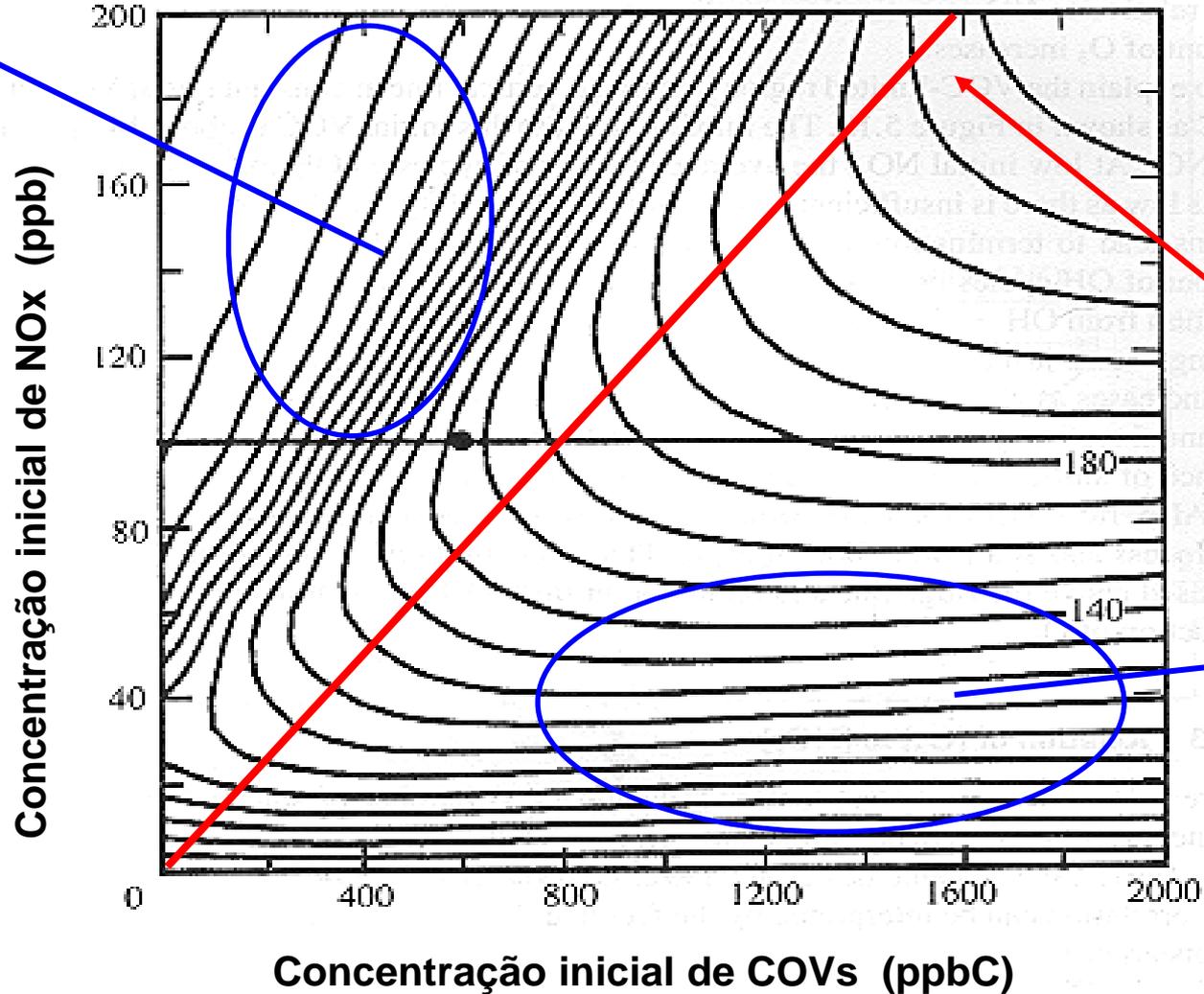
Incremento máximo de reatividade (MR) de alguns COVs (massa de O₃ produzido por massa de COV)



Isopletas de concentração de ozônio (ppb) baseadas em simulações químicas.

NO_x = (NO + NO₂) e COVs = compostos orgânicos voláteis (pg. 237, Seinfeld & Pandis, 2006)

Região
NO_x
saturada



razão
COV:NO_x ~ 8:1

Região
sensível
ao NO_x

TABLE 6.3 Generalized VOC/NO_x Mechanism

| Reaction | Rate Constant (298 K) |
|---|---|
| 1. $\text{RH} + \text{OH} \xrightarrow{\text{O}_2} \text{RO}_2 + \text{H}_2\text{O}$ | $26.3 \times 10^{-12}{}^a$ |
| 2. $\text{RO}_2 + \text{NO} \xrightarrow{\text{O}_2} \text{NO}_2 + \text{R}'\text{CHO} + \text{HO}_2$ | $7.7 \times 10^{-12}{}^b$ |
| 3. $\text{HO}_2 + \text{NO} \longrightarrow \text{NO}_2 + \text{OH}$ | 8.1×10^{-12} |
| 4. $\text{OH} + \text{NO}_2 \xrightarrow{\text{M}} \text{HNO}_3$ | 1.1×10^{-11} (at 1 atm) |
| 5. $\text{HO}_2 + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$ | 2.9×10^{-12} |
| 6. $\text{RO}_2 + \text{HO}_2 \longrightarrow \text{ROOH} + \text{O}_2$ | $5.2 \times 10^{-12}{}^c$ |
| 7. $\text{NO}_2 + h\nu \xrightarrow{\text{O}_2} \text{NO} + \text{O}_3$ | Depends on light intensity ^d |
| 8. $\text{O}_3 + \text{NO} \longrightarrow \text{NO}_2 + \text{O}_2$ | 1.9×10^{-14} |

^aRate coefficient for propene (Table B.4). Other reactions consider R equal to CH₃. Propene is selected because it is a relatively important constituent of the urban atmosphere. Even though OH-propene reaction proceeds by OH addition to the double bond of propene (Section 6.10.2), the net result after O₂ attack on the initial radical formed is a peroxy radical.

^bRate coefficient for CH₃O₂ + NO.

^cRate coefficient for CH₃O₂ + HO₂.

^dTypical photolysis rate coefficient for NO₂ is $j_{\text{NO}_2} = 0.015 \text{ s}^{-1}$.

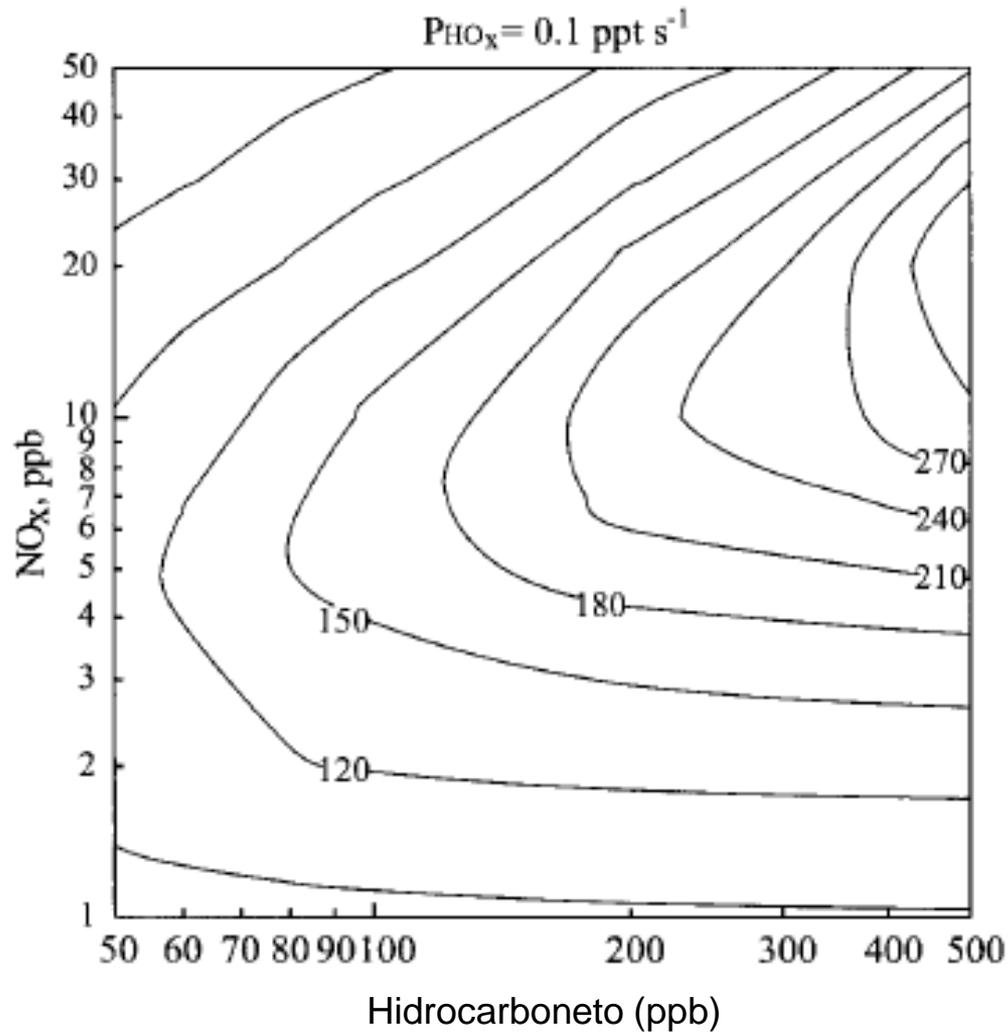
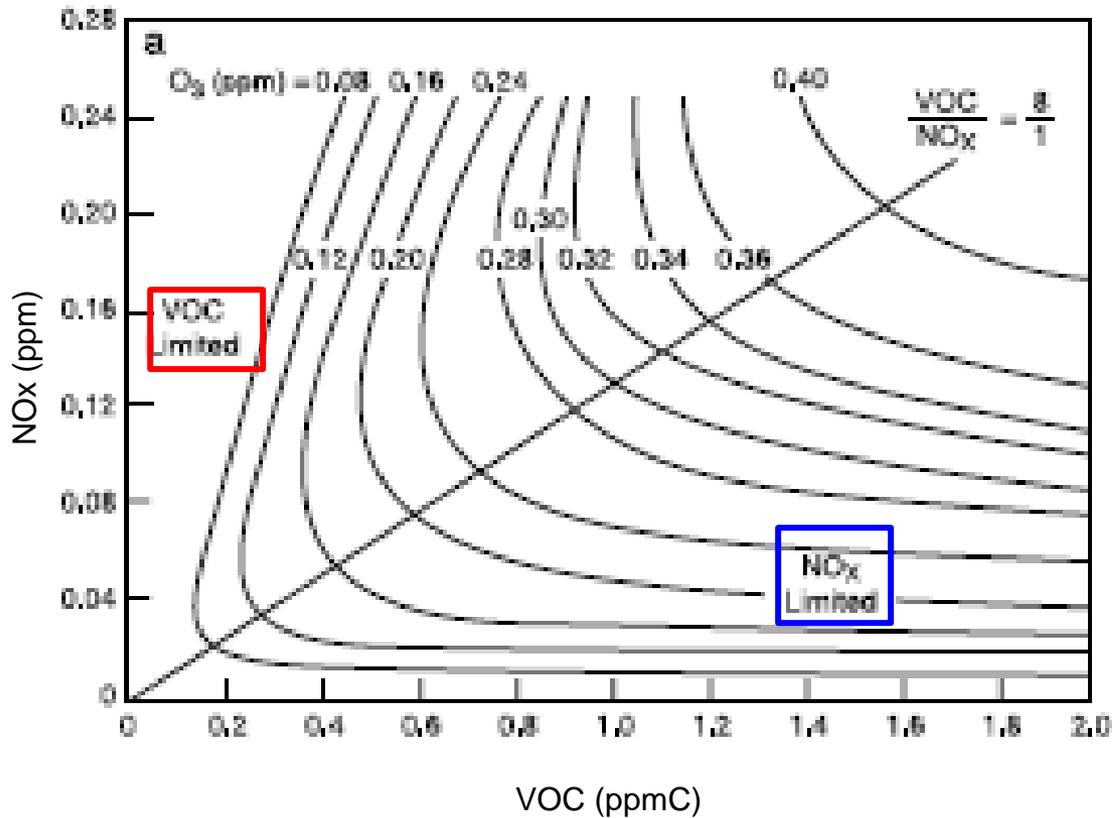
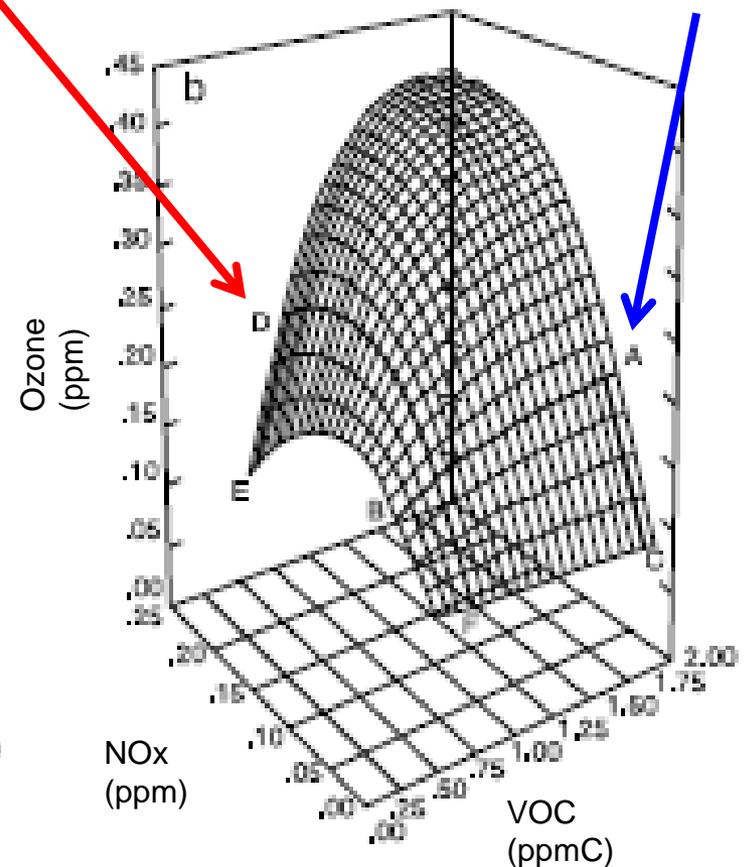


FIGURE 6.12 Isopleths of maximum O_3 mixing ratio achieved over a 10-h period by integrating the rate equations arising from the mechanism in Table 6.3.



COV-limitada, região urbana altamente poluída

NO_x-limitada, região suburbana ou rural



Isopletas típicas de picos de ozônio geradas a partir de misturas iniciais de COV e NO_x no ar:

- Representação bi-dimensional gerada a partir do modelo EKMA
- Representação tri-dimensional. A região **COV-limitante (D)** é encontrada em algumas regiões urbanas altamente poluídas, enquanto que a condição **NO_x-limitante (A)** é típica de regiões suburbanas e áreas rurais.

Resumo: os ingredientes

Para formar ozônio na troposfera, é preciso:

- **O próprio ozônio**
(sem ozônio → sem radical OH)
fonte: estratosfera
- **CO** e COV (compostos orgânicos voláteis)
fonte: emissões antropicas (queima de combustíveis fósseis) e naturais (queimadas de florestas)
- **NO_x**
fonte: emissões antropicas (queima de combustíveis fósseis) e naturais (relâmpagos)

Empirical Development of Ozone Isoleths: Applications to Los Angeles

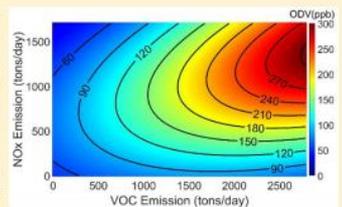
Yu Qian,[†] Lucas R. F. Henneman,[‡] James A. Mulholland,[†] and Armistead G. Russell^{*†}

[†]School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

[‡]Department of Biostatistics, Harvard T. H. Chan School of Public Health, Harvard University, Boston, Massachusetts 02115, United States

Supporting Information

ABSTRACT: Understanding quantitative relationships between ambient ozone concentrations and precursor emissions is important to policy-makers and stakeholders. Such relationships are often captured as ozone isopleth diagrams developed using air quality models. Model-based approaches have limitations, including errors stemming from uncertainties in inputs and modeled processes, and can be computationally burdensome. We develop and apply an empirical method based on ozone design values calculated in the South Coast Air Basin, California, for 1975–2016 to construct ozone isopleths. The study domain is the area with the highest ozone levels in the United States that has experienced high levels of emissions control. Quadratic and log-quadratic models were constructed, and both capture the actual observations very well ($R^2 \sim 0.98$) and re-create the general characteristics of traditional air quality model-generated isopleths. The empirical approach benefits from being based on observations that are highly accurate (but have a low spatial coverage). Analysis shows that uncertainties are <30% near likely future control levels. Furthermore, the method shows that the nitrogen oxide (NO_x)–volatile organic compound (VOC)–ozone system in the 1970s was in the region where VOC controls were most effective and then more recently moved to the region where both VOC and NO_x controls are effective.



1. INTRODUCTION

The response of ozone to changes in emissions of volatile organic compounds (VOCs) and nitrogen oxides (NO_x) has been derived using air quality models of varying complexity, from box models to fully three-dimensional chemical transport models (CTMs).^{1–8} While box models tend to focus on the chemistry driving the system, CTMs are developed to capture all of the major processes impacting ozone and related pollutants, including chemistry, emissions, transport, and deposition. Both provide information about the response of ozone to varying levels of NO_x and VOC.

A convenient representation of the relationship of ozone to VOC and NO_x levels (emissions or initial conditions) is the ozone isopleth (Figure 2) (or “EKMA” diagram).³ Such

$$C(x_0 + \Delta e_1, y_0 + \Delta e_2) = C(x_0, y_0) + \Delta e_1 S_{x_0}^{(1)}(x_0, y_0) + \Delta e_2 \times S_{y_0}^{(1)}(x_0, y_0) + \frac{\Delta e_1^2}{2} S_{x_0 x_0}^{(2)}(x_0, y_0) + \Delta e_1 \Delta e_2 S_{x_0 y_0}^{(2)}(x_0, y_0) + \frac{\Delta e_2^2}{2} S_{y_0 y_0}^{(2)}(x_0, y_0) + \frac{\Delta e_1^3}{6} S_{x_0 x_0 x_0}^{(3)}(x_0, y_0) + \frac{\Delta e_1^2 \Delta e_2}{2} S_{x_0 x_0 y_0}^{(3)}(x_0, y_0) + \frac{\Delta e_1 \Delta e_2^2}{2} S_{x_0 y_0 y_0}^{(3)}(x_0, y_0) + \frac{\Delta e_2^3}{6} S_{y_0 y_0 y_0}^{(3)}(x_0, y_0) + \dots \quad (1)$$

where x_0 and y_0 are the initial emissions of the precursors (tons per day), Δe_1 and Δe_2 are changes around x_0 and y_0 , respectively, C is the response concentration (parts per billion), and $S^{(i)}$ is the i th-order sensitivity (parts per billion per ton per day).¹⁰ In this case, the CTM, with a higher-order

Novel Method for Ozone Isoleth Construction and Diagnosis for the Ozone Control Strategy of Chinese Cities

Huizhong Shen,^{*†} Zhe Sun,[†] Yilin Chen, Armistead G. Russell, Yongtao Hu, Mehmet Talât Odman, Yu Qian, Alexander T. Archibald, and Shu Tao

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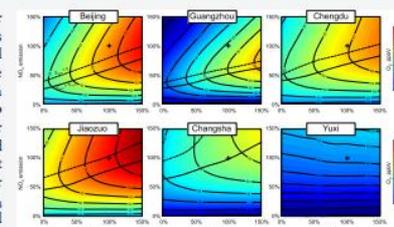
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Supporting Information

ABSTRACT: Ozone (O_3) isopleths describe the nonlinear responses of O_3 concentrations to changes in nitrogen oxides (NO_x) and volatile organic compounds (VOCs) and thus are pivotal to the determination of O_3 control requirements. In this study, we innovatively use the Community Multiscale Air Quality model with the high-order decoupled direct method (CMAQ-HDDM) to simulate O_3 pollution of China in 2017 and derive O_3 isopleths for individual cities. Our simulation covering the entire China Mainland suggests severe O_3 pollution as 97% of the residents experienced at least 1 day, in 2017, in excess of Chinese Level-II Ambient Air Quality Standards for O_3 as $160 \mu\text{g}\cdot\text{m}^{-3}$ (81.5 ppbV equally). The O_3 responses to emissions of precursors vary widely across individual cities. Densely populated metropolitan areas such as Jing-Jin-Ji, Yangtze River Delta, and Pearl River Delta are following NO_x -saturated regimes, where a small amount of NO_x reduction increases O_3 . Ambient O_3 pollution in the eastern region generally is limited by VOCs, while in the west by NO_x . The city-specific O_3 isopleths generated in this study are instrumental in forming hybrid and differentiated strategies for O_3 abatement in China.

KEYWORDS: air pollution, ozone isopleth, ozone abatement, EKMA, CMAQ-HDDM, decoupled direct method, nitrogen oxide, volatile organic compounds



■ INTRODUCTION

Tropospheric ozone (O_3) is a trace gas and major air pollutant with adverse impacts on human and ecosystem health.¹ Human exposure to O_3 is associated with increased risks of respiratory and circulatory disease and premature death.^{1–3} Elevated ground-level O_3 also reduces crop production and warms the atmosphere.⁴ China is experiencing worsening O_3 pollution in recent years.⁵ The Global Burden of Disease reported 1.8×10^5 premature deaths in China in 2017 from exposure to ambient O_3 , which is the highest among all countries (and the third highest in terms of the attributable mortality rate).⁶ Both large-scale surface measurements and satellite observations show that O_3 levels in China are generally 7.8–10.0 ppbV in excess of the WHO guideline that is densely

because “ NO_x titration” is reduced.^{14,15} This O_3 – NO_x –VOC relationship conforms to a general pattern and can be illustrated with an isoplethic diagram, referred to as “ O_3 isopleth”, where emissions or initial concentrations of NO_x and VOCs define two different axes perpendicular to each other, and the corresponding O_3 levels form the isopleths.^{16–18} O_3 isopleths are widely used as a basis to diagnose O_3 trends in response to precursors’ emission changes¹⁹ and are key to the development of control strategies for O_3 reduction.²⁰

There are two major conventional approaches to draw O_3 isopleths for a given locality: (1) developing empirical relationships based on observational data,^{21–23} or more commonly, (2) predicting O_3 changes using numerical models.^{26–33} While empirical approaches can be fast and



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Emission source-based ozone isopleth and isosurface diagrams and their significance in ozone pollution control strategies

Huihong Luo^{1,**}, Kaihui Zhao^{1,**}, Zibing Yuan^{1,*}, Leifeng Yang¹, Junyu Zheng², Zhijiong Huang², Xiaobo Huang³

¹School of Environment and Energy, South China University of Technology, Guangzhou 510006, China

²Institute of Environmental and Climate Research, Jinan University, Guangzhou 510632, China

³Shenzhen Academy of Environmental Sciences, Shenzhen 518022, China

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ABSTRACT

In the past decade, ozone (O_3) pollution has been continuously worsening in most developing countries. The accurate identification of the nonlinear relationship between O_3 and its precursors is a prerequisite for formulating effective O_3 control measures. At present, precursor-based O_3 isopleth diagrams are widely used to infer O_3 control strategy at a particular location. However, there is frequently a large gap between the O_3 -precursor nonlinearity delineated by the O_3 isopleths and the emission source control measures to reduce O_3 levels. Consequently, we developed an emission source-based O_3 isopleth diagram that directly illustrates the O_3 level changes in response to synergistic control on two types of emission sources using a validated numerical modeling system and the latest regional emission inventory. Isopleths can be further upgraded to isosurfaces when co-control on three types



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Adjoint-based computation of U.S. nationwide ozone exposure isopleths



Akshay Ashok*, Steven R.H. Barrett

Laboratory for Aviation and the Environment, Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, United States

HIGHLIGHTS

- We create O₃ exposure isopleths everywhere in the US using adjoint sensitivities.
- NO_x emissions lower O₃ for 51% of the year on average at 29% of locations in 2006.
- The isopleth ridge line VOC/NO_x ratio is 9.2 ppbC/ppb on average across grid cells.
- Ozone-neutral VOC/NO_x emission ratios are 0.01–1.9 ppbC/ppb across grid cells.

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ABSTRACT

Population exposure to daily maximum ozone is associated with an increased risk of premature mortality, and efforts to mitigate these impacts involve reducing emissions of nitrogen oxides (NO_x) and volatile organic compounds (VOCs). We quantify the dependence of U.S. national exposure to annually averaged daily maximum ozone on ambient VOC and NO_x concentrations through ozone exposure isopleths, developed using emissions sensitivities from the adjoint of the GEOS-Chem air quality model for 2006. We develop exposure isopleths for all locations within the contiguous US and derive metrics based on the isopleths that quantify the impact of emissions on national ozone exposure. This work is the first to create ozone exposure isopleths using adjoint sensitivities and at a large scale. We find that across the US, 29% of locations experience VOC-limited conditions (where increased NO_x emissions lower ozone) during 51% of the year on average. VOC-limited conditions are approximately evenly distributed diurnally



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Diurnal regulation of VOCs may not be effective in controlling ozone pollution in China

Weiling Wu^a, Wenbo Xue^{a,b,*}, Yixuan Zheng^a, Yanli Wang^a, Yu Lei^{a,**}, Jinnan Wang^a

^a Chinese Academy of Environmental Planning, Beijing, 100012, China

^b State Environmental Protection Key Laboratory of Environmental Planning and Policy Simulation, Chinese Academy of Environmental Planning, Beijing, 100012, China

HIGHLIGHTS

- VOCs diurnal regulation may not be effective in controlling O₃ at the regional scale.
- VOCs diurnal regulation had minor influence on hourly peak O₃ concentration.
- Positive or negative impacts on O₃ concentrations were both found at the city level.

ARTICLE INFO

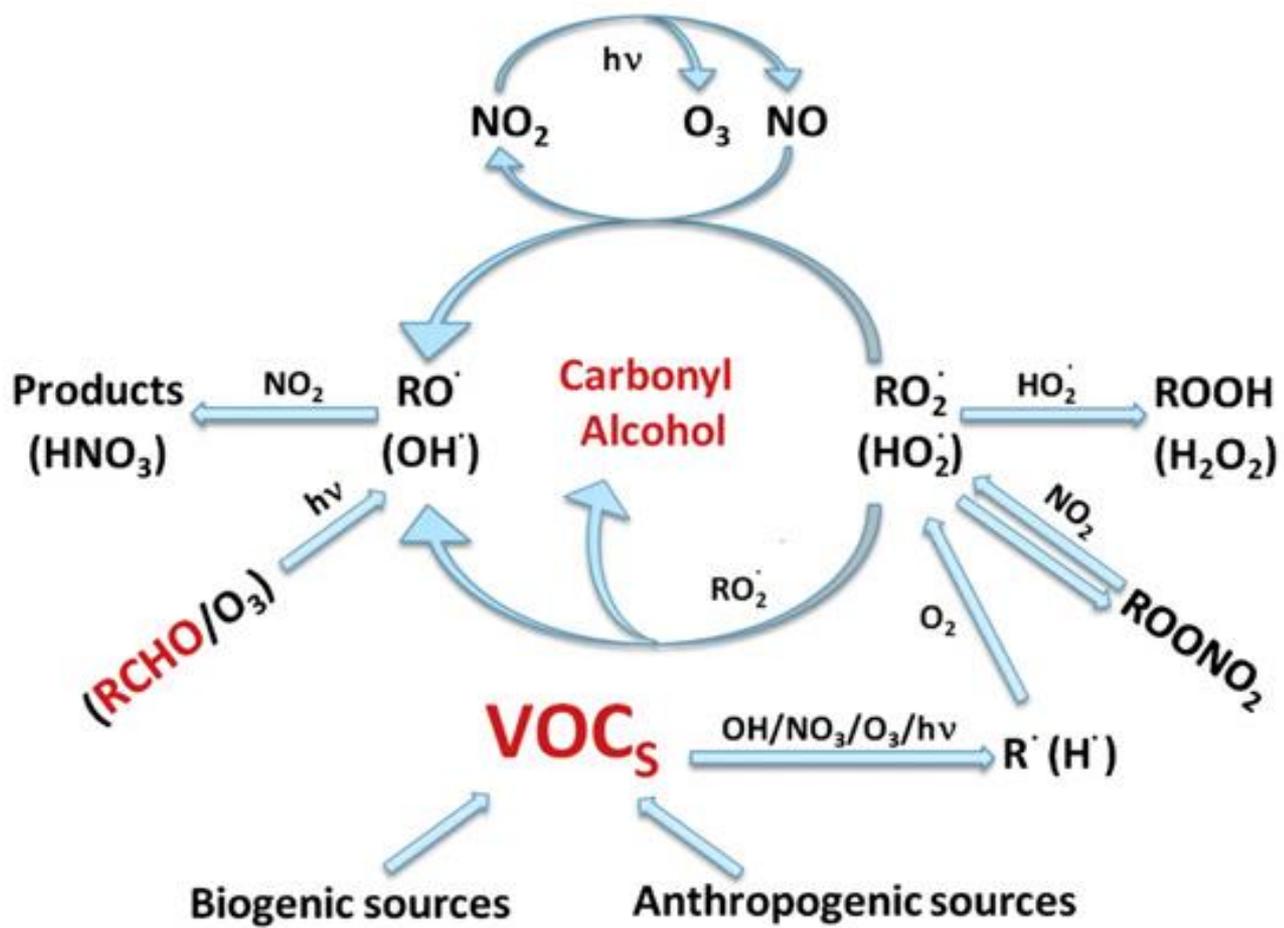
Keywords:

Ozone pollution
VOCs diurnal Regulation
WRF-CAMx air quality model

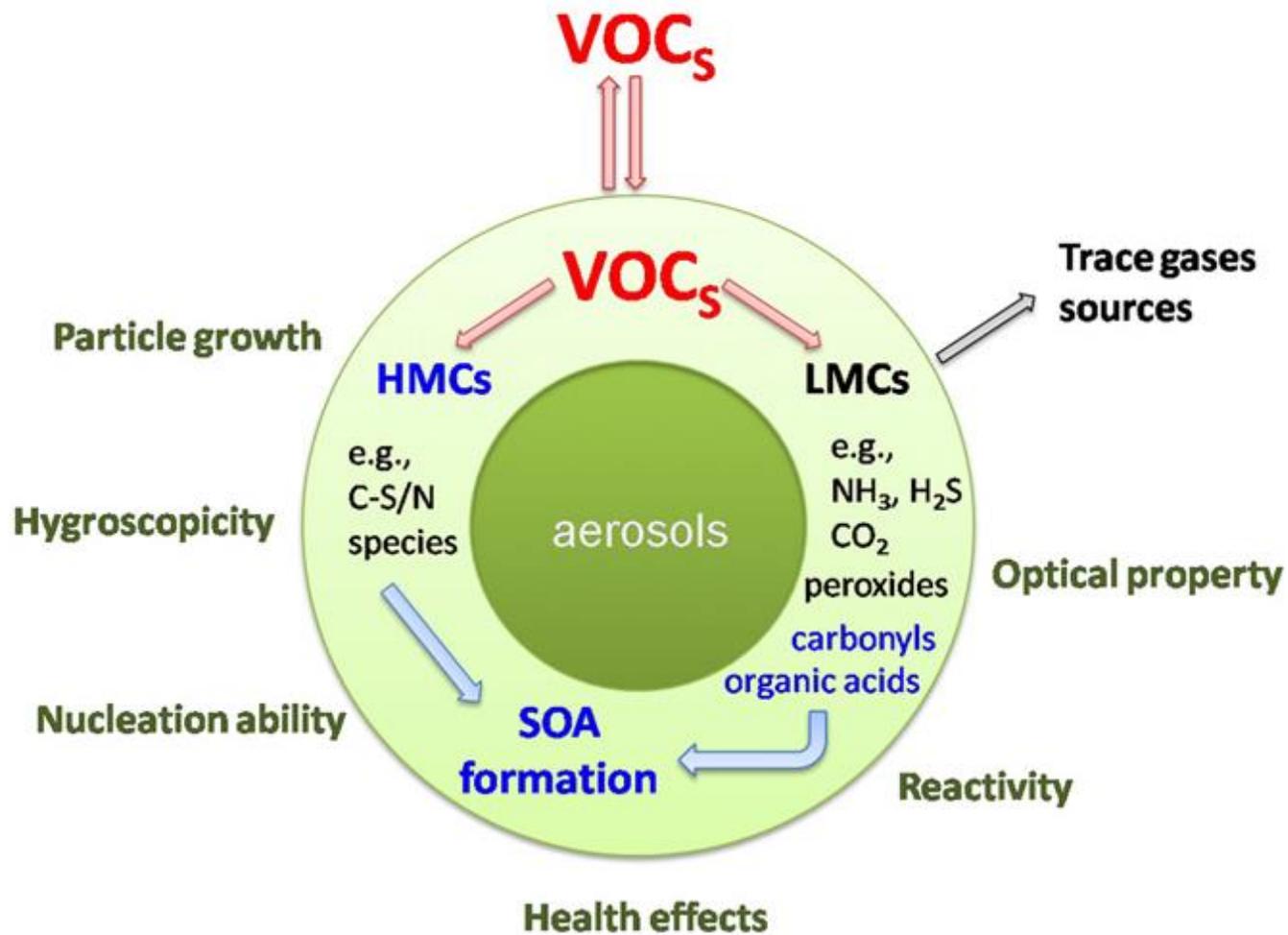
ABSTRACT

Over the past few years, marked increases in ground-level ozone (O₃) concentration has been detected over much of eastern China. These high levels of O₃ pollution have been demonstrated to be detrimental to human health and plant growth, which requires urgent control on China's O₃ pollution. Among the various control measures, diurnal regulations of VOCs were adopted in some regions in China. For example, several local governments encourage factories with notable VOCs emissions shift their manufacturing processes to the nighttime; some governments also offer discount for night refueling. However, the effects of this diurnal regulation approach are still unclear. To evaluate the effectiveness of this measure, we proposed a quantitative assessment using WRF-CAMx air quality model. The assessment was systematically implemented at multiple time and spatial scales. Results at the regional scale revealed that the diurnal regulation of VOCs could slightly redistribute hourly O₃ concentrations and had minor influence on hourly peak O₃ concentration. The effects of this measure on hourly O₃ concentrations varied substantially across different cities: positive or negative impacts on O₃ concentrations were both found at the city level. At the daily scale, the variations of maximum daily 8-h average (MDA8) O₃

COVs: processos em fase gasosa



COVs: reações heterogêneas



HMCs: high molecular weight compounds; LMCs: low molecular weight compounds

Fatores que favorecem o *smog* fotoquímico:

- altas concentrações de poluentes primários (e.x., NO, COVs),
- poucas nuvens, permitindo alta intensidade de raios UV,
- inversões atmosféricas (e.x., São Paulo e Los Angeles),
- ventos fracos incapazes de dispersar poluentes.

Os processos que levam a formação de níveis elevados de O₃,
produzem também acidez atmosférica e material particulado.

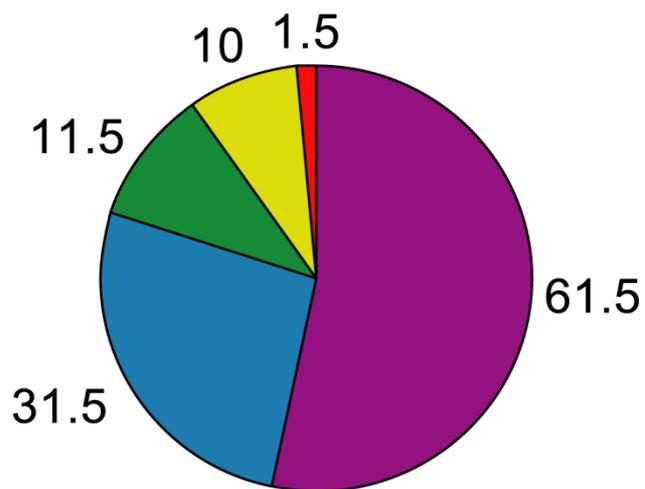
Questões:

No Brasil altas concentrações de acetaldeído e PAN tem sido medidas na atmosfera urbana, o que tem sido atribuído ao uso de etanol como combustível. Mostrar as reações que poderiam explicar esta condição.

Construir um mecanismo que mostra que o **éter metil terc-butílico** ou **éter metil terciário butílico** (MTBE), aditivo adicionado na gasolina, sofre oxidação na atmosfera produzindo formaldeído bem como acetona, formiato terc-butílico ($\text{HC(O)OC(CH}_3)_3$) e acetato de metila ($\text{CH}_3\text{C(O)OCH}_3$).

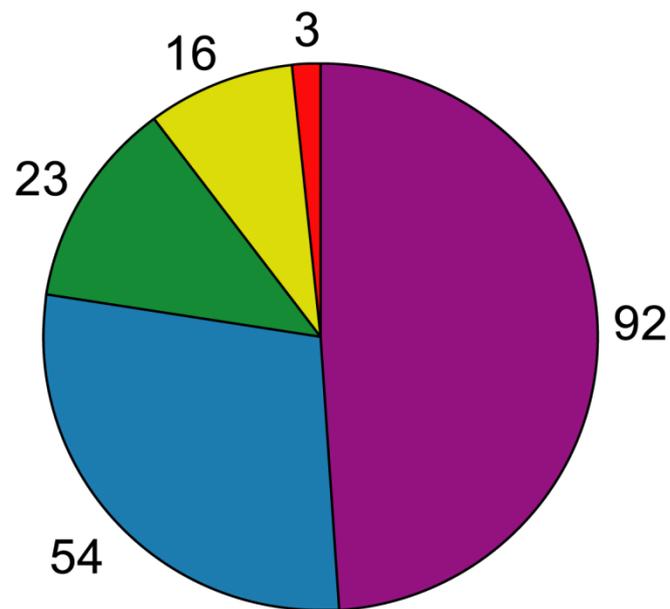
Mudança da capacidade oxidante da atmosfera

Pre-industrial

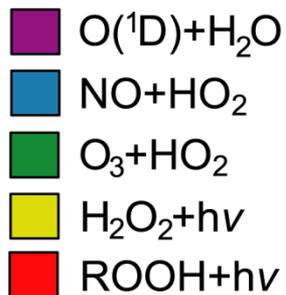


Total 116 Tmol/year

Present



Total 188 Tmol/year



Bibliografia:

C. Baird. “Química Ambiental”, 2a.ed., Bookman, Porto Alegre, 2002.

D.J. Jacob, “Introduction to Atmospheric Chemistry”, Princeton University Press, Princeton, 1999.

B.J. Finlayson-Pitts, J.N. Pitts Jr., “Chemistry of the upper and lower atmosphere – theory, experiments and applications, Academic Press, San Diego, 1998.

Brasseur, G.P., Orlando, J.J., Tyndall, G.S., Atmospheric Chemistry and Global Change, Oxford University Press, New York, 1999.

J.H. Seinfeld e S. N. Pandis, "Atmospheric Chemistry and Physics: from air pollution to climate change", John Wiley & Sons, New York, 1998.

<http://www.abema.org.br/> (Associação Brasileira de Entidades Estaduais de Meio Ambiente)

<http://www.cetesb.sp.gov.br/>

<http://www.epa.gov/air/>

Do, D.H.; Langenhove, H.V.; Walgraeve, C.; Hayleeyesus, S.F.; Wispelaere, P.D.; Dewulf, J.; Demeestere, K., 2013: Volatile organic compounds in an urban environment: a comparison among Belgium, Vietnam and Ethiopia, *International Journal of Environmental Analytical Chemistry*, 93(3), 298-314.

Kesselmeier, J., Staudt, M., 1999. Biogenic volatile organic compounds (VOC): An overview on emission, physiology and ecology, *Journal of Atmospheric Chemistry*, 33, 23–88.

Maka, P. A.; Moran, M. D.; Scholtz, M. T.; Taylor, A., 2003. Speciation of volatile organic compound emissions for regional air quality modeling of particulate matter and ozone, *Journal of Geophysical Research: Atmospheres*, 108 (D2), ACH 2-1–ACH 2-51.

Martins, L.D.; Andrade, M.F.; Freitas, E.D.; Pretto, A.; Gatti, L.V.; Albuquerque, E.L.; Tomaz, E.; Guardani, M.L.; Martins, M.H.R.B.; Junior, O.M.A., 2006. Emission factors for gas-powered vehicles traveling through road tunnels in São Paulo, Brazil, *Environ. Sci. Technol*, 40, 6722-6729.

Penuelas, J.; Staudt, M., 2010. BVOCs and global change, *Trends in Plants Science*, 15(3), 133-144.