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**Gas-phase Tropospheric Chemistry
of Organic Compounds**

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over the temperature range 293–599 K, with a 298 K rate constant of $3.27 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is unchanged.

1-Propanol. The rate constants of Nelson *et al.*¹⁸ and Tully¹⁹ are given in Table 41. These rate constants are in reasonable agreement with the previous recommendation of Atkinson,¹ and a unit-weighted average of the rate constants of Overend and Paraskevopoulos,⁴³ Wallington and Kurylo,⁴⁶ Nelson *et al.*¹⁸ and Tully¹⁹ leads to the recommendation of

$$k(1\text{-propanol}) = 5.53 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of $\pm 30\%$. This recommendation supersedes that previously recommended by Atkinson¹ of $5.34 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, using the rate constants of Overend and Paraskevopoulos⁴³ and Wallington and Kurylo.⁴⁶

2-Propanol. The rate constants of Nelson *et al.*¹⁸ and Tully¹⁹ are given in Table 41 and are plotted in Arrhenius form, together with the rate constants of Overend and Paraskevopoulos⁴³ and Wallington and Kurylo,⁴⁶ in Fig. 38. A unit-weighted least-squares analysis of the absolute rate constants of Overend and Paraskevopoulos,⁴³ Wallington and Kurylo,⁴⁶ Nelson *et al.*¹⁸ and Tully¹⁹ and the relative rate constant of Nelson *et al.*,¹⁸ using the expression $k = CT^2 e^{-D/T}$, yields the recommendation of

$$k(2\text{-propanol}) = (7.21_{-1.95}^{+2.67}) \times 10^{-18} T^2 e^{(631 \pm 98)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

$$k(2\text{-propanol}) = 5.32 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 35\%$. This recommended expression is similar to that of Atkinson¹ of

$$k(2\text{-propanol}) = 7.32 \times 10^{-18} T^2 e^{620/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 240–440 K, with a 298 K rate constant of $5.21 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

1-Butanol. The room temperature rate constants of Nelson *et al.*¹⁸ and Tully¹⁹ are given in Table 41. A unit-weighted average of the absolute rate constants of Wallington and Kurylo,⁴⁶ Nelson *et al.*¹⁸ and Tully¹⁹ and the relative rate constant of Nelson *et al.*¹⁸ leads to the recommendation of

$$k(1\text{-butanol}) = 8.57 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of $\pm 35\%$.

1-Pentanol, 1-Hexanol and 1-Heptanol. The rate constants of Nelson *et al.*¹⁸ are given in Table 41. These rate constants of Nelson *et al.*¹⁸ are in good agreement with the absolute room temperature rate constants of Walling-

ton and Kurylo⁴⁶ for 1-pentanol and Wallington *et al.*⁵⁰ for 1-hexanol and 1-heptanol. Unit-weighted least-squares averages of the rate constants of Wallington and Kurylo⁴⁶ (for 1-pentanol), Wallington *et al.*⁵⁰ (for 1-hexanol and 1-heptanol) and Nelson *et al.*¹⁸ lead to the recommendations of

$$k(1\text{-pentanol}) = 1.11 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

$$k(1\text{-hexanol}) = 1.25 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ and}$$

$$k(1\text{-heptanol}) = 1.37 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

all at 298 K and with estimated overall uncertainties of $\pm 35\%$.

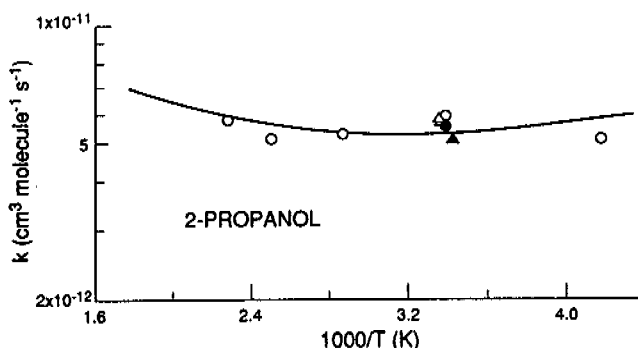


FIG. 38. Arrhenius plot of selected rate constants for the reaction of the OH radical with 2-propanol. (●) Overend and Paraskevopoulos;⁴³ (○) Wallington and Kurylo;⁴⁶ (△) Nelson *et al.*;¹⁸ (▲) Tully;¹⁹ (—) recommendation (see text).

3.6.5. Ethers

Dimethyl ether. The room temperature rate constants of Wallington *et al.*²¹ and Nelson *et al.*¹⁸ are given in Table 41. These rate constants range over a factor of 1.4, and are reasonably consistent with the previous recommendation of Atkinson¹ of

$$k(\text{dimethyl ether}) = 1.04 \times 10^{-11} e^{-372/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 295–442 K, with a 298 K rate constant of $2.98 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This previous recommendation¹ is hence unchanged.

Diethyl ether. The absolute rate constant of Nelson *et al.*¹⁸ and the relative rate constants of Bennett and Kerr,²² Nelson *et al.*¹⁸ and Semadeni *et al.*²³ are given in Table 41 and those of Nelson *et al.*¹⁸ and Bennett and Kerr²² are plotted, together with the rate constants of Tully and Droege,⁵¹ Wallington *et al.*⁵² and Bennett and Kerr,⁵³ in Fig. 39. There is a significant amount of scatter between the data from the various studies, with the rate constants of Bennett and Kerr,²² obtained relative to the rate constant for the reaction of the OH radical with 2,3-dimethylbutane, being $\sim 30\%$ lower than the absolute rate constants of Tully and Droege⁵¹ and Wallington *et al.*⁵² The relative rate constants of Semadeni *et al.*²³ are in good agreement with ($\sim 10\%$ lower than) those of

Tully and Droege⁵¹ and Wallington *et al.*⁵² A unit-weighted least-squares analysis of the absolute rate constants of Tully and Droege,⁵¹ Wallington *et al.*⁵² and Nelson *et al.*¹⁸ and the relative rate constant of Nelson *et al.*¹⁸ using the expression $k = CT^2 e^{-D/T}$, leads to the recommendation of

$$k(\text{diethyl ether}) = (8.91^{+2.1}_{-1.1}) \times 10^{-18} T^2 e^{(837 \pm 70)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–442 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{diethyl ether}) = 1.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 35\%$. This recommendation supersedes, but is similar to, that of Atkinson¹ of

$$k(\text{diethyl ether}) = 8.80 \times 10^{-18} T^2 e^{844/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 240–442 K, with a 298 K rate constant of $1.33 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

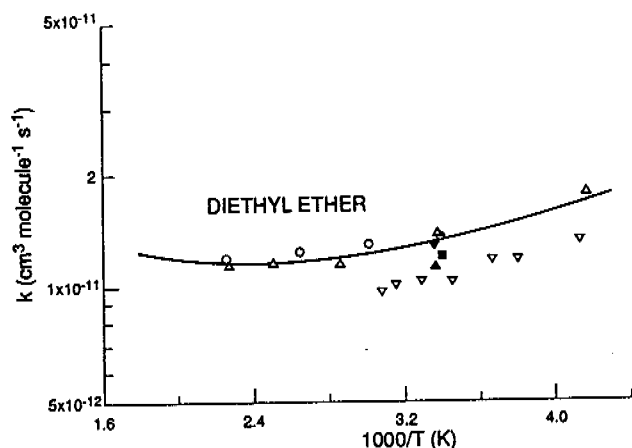


FIG. 39. Arrhenius plot of selected rate constants for the reaction of the OH radical with diethyl ether. (○) Tully and Droege;⁵¹ (△) Wallington *et al.*⁵² (■) Bennett and Kerr;⁵³ (▲) Nelson *et al.*¹⁸ absolute rate constant; (▼) Nelson *et al.*¹⁸ relative rate constant; (▽) Bennett and Kerr;²² (—) recommendation (see text).

Di-n-propyl ether. The rate constants of Wallington *et al.*²¹ Bennett and Kerr²² and Nelson *et al.*¹⁸ are given in Table 41 and are plotted, together with the rate constants of Wallington *et al.*⁵² and Bennett and Kerr,⁵³ in Arrhenius form in Fig. 40. The rate constants of Wallington *et al.*²¹ Bennett and Kerr²² and Nelson *et al.*¹⁸ especially those of Bennett and Kerr,²² are higher than the previously reported rate constants of Wallington *et al.*⁵² and Bennett and Kerr.⁵³ A unit-weighted least-squares analysis of the absolute rate constants of Wallington *et al.*⁵² and Nelson *et al.*¹⁸ and the relative rate constants of

Wallington *et al.*²¹ and Nelson *et al.*¹⁸ using the expression $k = CT^2 e^{-D/T}$, leads to the recommendation of

$$k(\text{di-}n\text{-propyl ether}) = (1.31^{+0.39}_{-0.30}) \times 10^{-17} T^2 e^{(825 \pm 80)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{di-}n\text{-propyl ether}) = 1.85 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

at 298 K, with an estimated overall uncertainty at 298 K of $\pm 40\%$. This recommendation is slightly different from the previous recommendation of Atkinson¹ of

$$k(\text{di-}n\text{-propyl ether}) = 1.42 \times 10^{-17} T^2 e^{778/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range, with a 298 K rate constant of $1.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

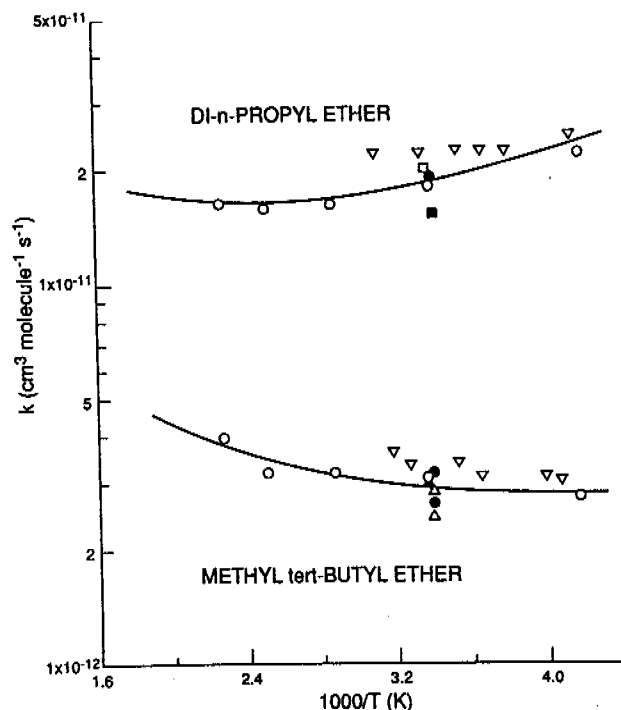


FIG. 40. Arrhenius plots of selected rate constants for the reactions of the OH radical with di-*n*-propyl ether and methyl *tert*-butyl ether. (○) Wallington *et al.*⁵² (for di-*n*-propyl ether) and Wallington *et al.*⁵⁴ (for methyl *tert*-butyl ether); (■) Bennett and Kerr;⁵³ (△) Cox and Goldstone;⁵⁵ (●) Wallington *et al.*²¹ (□) Nelson *et al.*¹⁸ (▽) Bennett and Kerr;²² (▲) Smith *et al.*²⁴ (—) recommendations (see text).

Methyl tert-butyl ether. The rate constants of Wallington *et al.*²¹ Bennett and Kerr²² and Smith *et al.*²⁴ are given in Table 41 and are plotted, together with those of Wallington *et al.*⁵⁴ and Cox and Goldstone,⁵⁵ in Arrhenius form in Fig. 40. As for di-*n*-propyl ether, the rate constants of Bennett and Kerr²² are consistently higher than those of

Wallington *et al.*,^{21,54} Cox and Goldstone⁵⁵ and Smith *et al.*²⁴ A unit-weighted least-squares analysis of the absolute rate constants of Wallington *et al.*⁵⁴ and the relative rate constants of Wallington *et al.*²¹ and Smith *et al.*,²⁴ using the expression $k = CT^2 e^{-D/T}$, leads to the recommendation of

$$k(\text{methyl } tert\text{-butyl ether}) = (6.54 \pm 1.61) \times 10^{-18} T^2 e^{(483 \pm 88)/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 240–440 K, where the indicated errors are two least-squares standard deviations, and

$$k(\text{methyl } tert\text{-butyl ether}) = 2.94 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty at 298 K of $\pm 40\%$. This recommendation supersedes that of Atkinson¹ of

$$k(\text{methyl } tert\text{-butyl ether}) = 6.81 \times 10^{-18} T^2 e^{460/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the same temperature range of 240–440 K, with a 298 K rate constant of $2.83 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

Methyl n-butyl ether, ethyl n-butyl ether, ethyl tert-butyl ether, di-n-butyl ether and di-n-pentyl ether. The rate constants of Wallington *et al.*,²¹ Bennett and Kerr²² (ethyl *n*-butyl ether and ethyl *tert*-butyl ether), Nelson *et al.*¹⁸ (ethyl *n*-butyl ether, di-*n*-butyl ether and di-*n*-pentyl ether), Smith *et al.*²⁵ (ethyl *tert*-butyl ether) and Semadeni *et al.*²³ (methyl *n*-butyl ether, ethyl *n*-butyl ether, di-*n*-butyl ether and di-*n*-pentyl ether) are given in Table 41. For di-*n*-pentyl ether, Semadeni *et al.*²³ determined rate constants relative to those for di-*n*-butyl ether over the temperature range 263–373 K; only the 298 K rate constant is given in Table 41 since no temperature dependent recommendation is given for di-*n*-butyl ether. The absolute and relative rate constants of Wallington *et al.*,^{21,50,52} Nelson *et al.*,¹⁸ Smith *et al.*²⁵ and Semadeni *et al.*²³ are in good agreement, while the relative rate constants of Bennett and Kerr^{22,53} are generally significantly lower. The following recommendations are made from unit-weighted averages:

$$k(\text{methyl } n\text{-butyl ether}) = 1.48 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

based on the rate constants of Wallington *et al.*,^{21,50} and Semadeni *et al.*,²³

$$k(\text{ethyl } n\text{-butyl ether}) = 2.13 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

based on the rate constants of Wallington *et al.*,^{21,50} Nelson *et al.*¹⁸ and Semadeni *et al.*,²³

$$k(\text{ethyl } tert\text{-butyl ether}) = 8.84 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

based on the rate constants of Wallington *et al.*,^{21,50} and Smith *et al.*,²⁵

$$k(\text{di-}n\text{-butyl ether}) = 2.88 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

based on the rate constants of Wallington *et al.*,^{21,52} Nelson *et al.*¹⁸ and Semadeni *et al.*,²³ and

$$k(\text{di-}n\text{-pentyl ether}) = 3.32 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

based on the rate constants of Wallington *et al.*,^{21,52} Nelson *et al.*¹⁸ and Semadeni *et al.*,²³ all at 298 K and with estimated overall uncertainties of $\pm \sim 35\%$.

Furan. The room temperature rate constant of Bierbach *et al.*³⁰ is given in Table 41. This rate constant is in excellent agreement with the previously recommended¹ value of $4.02 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K. The previous recommendation of Atkinson¹ of

$$k(\text{furan}) = 1.32 \times 10^{-11} e^{334/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

over the temperature range 254–424 K, with a 298 K rate constant of $4.05 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is hence unchanged.

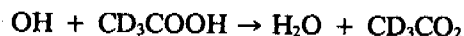
3.6.6. Carboxylic acids

Acetic Acid. The absolute rate constants of Singleton *et al.*³¹ for the reactions of the OH radical with CH_3COOH , CD_3COOH and CD_3COOD are given in Table 41. While the room temperature rate constant of Singleton *et al.*³¹ for CH_3COOH is in reasonable agreement with the previous measurement of Dagaut *et al.*,⁵⁶ the rate constants of Singleton *et al.*³¹ for CH_3COOH decrease with increasing temperature, in contrast to the study of Dagaut *et al.*⁵⁶ in which the rate constants increased with increasing temperature. A unit-weighted average of the room temperature rate constants from these two studies^{31,56} leads to the recommendation of

$$k(\text{acetic acid}) = 8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of a factor of 1.5. No temperature dependence is recommended.

Singleton *et al.*³¹ determined that the rate constant for the reaction of the OH radical with CD_3COOH is essentially identical to that for CH_3COOH , and that the rate constant for the reaction of the OH radical with CD_3COOD is uniformly a factor of ~ 3.5 lower than those for CH_3COOH and CD_3COOH over the temperature range 297–445 K. These observations indicate that the reaction proceeds by H- (or D-) atom abstraction from the -OH (or -OD) bond. For example, for CD_3COOH



Propionic acid. The absolute rate constants of Singleton *et al.*³¹ are given in Table 41. In this case, the agreement of the rate constants of Singleton *et al.*³¹ with those of Dagaut *et al.*⁵⁶ and Zetzsch and Stuhl⁵⁷ is reasonable. Both of the temperature dependent studies of Dagaut