Hydrogen Abstraction from Dimethyl Sulfide by Trifluoromethyl Radicals

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Abstract

Additional data are presented for hydrogen abstraction from $(CH_3)_2S$ by CF_3 radicals

$$CF_3 + (CH_3)_2S \rightarrow CF_3H + CH_3SCH_2 \tag{1}$$

leading to a revised value for the rate constant (k in $cm^3\ mol^{-1}\ s^{-1}$, E in $J\ mol^{-1}$):

$$\log k_1 = (11\cdot 83 \pm 0\cdot 06) - (26910 \pm 450)/19\cdot 145T$$

Combination of these results with thermochemical data gives a revised value of

$$\log k_{-1} = 11\cdot 9 - 61800/19\cdot 145T$$

for the rate constant of the reverse reaction.

In this communication we present additional data on hydrogen abstraction from $(CH_3)_2S$ by CF_3 radicals, data which were not included in our original paper on this reaction.[1]

The experimental work involved measuring rate constants for CF_3 radical attack on $(CH_3)_2S$

$$CF_3 + (CH_3)_2S \rightarrow CF_3H + CH_3SCH_2 \tag{1}$$

relative to the rate of recombination of CF_3 radicals

$$2CF_3 \rightarrow C_2F_6 \tag{2}$$

and in our paper we reported values of $k_1/k_2^{1/2}$ in the temperature range 79–167°. We had also collected some data at several other temperatures, both above and below this range, but, because the values of these rate constants deviated markedly from the remainder of the data, we did not consider them sufficiently reliable to be used in evaluating the Arrhenius parameters for the reaction.

Recently, however, we reexamined the omitted data and found that an error had been made in our original evaluation of the rate constants, and that the corrected values agreed well with those previously reported. The complete set of results, which now extends over a much wider temperature range (42–188°), is given in Table 1. The rate constants exhibit a high degree of reproducibility, and the corresponding Arrhenius plot shows a slight curvature, similar to that observed by Kibby and

[1] Arthur, N. L., and Yeo, K. S., *Aust. J. Chem.*, 1972, **25**, 803.

Weston for $CF_3 + H_2$.[2] A conventional least-squares analysis of the data (assuming $k_2 = 10^{13 \cdot 36}$ cm^3 mol^{-1} s^{-1}) gives

$$\log k_1 = (11 \cdot 83 \pm 0 \cdot 06) - (26910 \pm 450)/19 \cdot 145T$$

where k_1 is in cm^3 mol^{-1} s^{-1}, E is in J mol^{-1}, and the errors are standard deviations.

Table 1. Rate constants for abstraction of hydrogen atoms from $(CH_3)_2S$ by CF_3 radicals

k_1 and k_2 in cm^3 mol^{-1} s^{-1}

Temp. (°C)	41·7[A]	42·1[A]	42·2[A]	52·5[A]	68·0[A]	79·2	79·3	85·7	93·9	102·7
$k_1/k_2^{1/2}$	5·650	5·254	5·342	7·083	11·10	13·10	13·28	15·54	19·02	23·41
Temp. (°C)	118·0	133·8	149·0	163·2	164·0	164·3	166·8	187·6	188·5	
$k_1/k_2^{1/2}$	35·16	49·03	66·20	84·98	88·84	86·57	91·26	139·8[A]	145·5[A]	

[A] Not included in original paper.

The values of the pre-exponential factor and the activation energy are both lower than those we reported previously ($\log A$ 12·05, E 28·71 kJ mol^{-1}), and the relationship between the Arrhenius parameters for this reaction, and those for the corresponding reaction of CH_3 radicals, is therefore altered. Gray, Herod and Jones,[3] and Arthur and Bell,[4] have pointed out that the most reliable data for CH_3 and CF_3 attack on the same substrate give an A factor ratio, A_{CF_3}/A_{CH_3}, which is close to unity, and that the difference in reactivities of the two radicals is a consequence of a difference in activation energies, $E_{CH_3} - E_{CF_3}$. When the Arrhenius parameters reported by Arthur and Lee[5] for $CH_3 + (CH_3)_2S$ are combined with our previous values for $CF_3 + (CH_3)_2S$, the values of A_{CF_3}/A_{CH_3} and $E_{CH_3} - E_{CF_3}$ are 2·7 and 9·6 kJ mol^{-1}, respectively; the corresponding values obtained when the revised Arrhenius parameters for the CF_3 reaction are used are 1·62 and 11·4 kJ mol^{-1}. The ratio of rate constants, k_{CF_3}/k_{CH_3}, is therefore 51 at 400 K, and this is mainly due to the difference in activation energies for the two reactions, in accordance with the established trend.

In our original paper, we combined our results with thermochemical data in order to calculate Arrhenius parameters for the reverse reaction:

$$CH_3SCH_2 + CF_3H \rightarrow CH_3SCH_3 + CF_3 \qquad (-1)$$
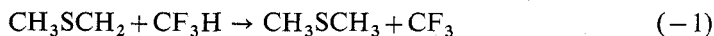
On the basis of our original results, the $\log A$ and E values deduced for this reaction were 12·2 and 62·6 kJ mol^{-1}, respectively.[1] If the revised values of the Arrhenius parameters are used together with the thermodynamic data listed by Arthur and Lee,[5] the rate constant for reaction (-1) is now given by

$$\log k_{-1} = 11 \cdot 9 - 61800/19 \cdot 145T$$

where k_{-1} is in cm^3 mol^{-1} s^{-1} and E is in J mol^{-1}.

[2] Kibby, C. L., and Weston, R. E., Jr, *J. Chem. Phys.*, 1968, **49**, 4825.
[3] Gray, P., Herod, A. A., and Jones, A., *Chem. Rev.*, 1971, **71**, 247.
[4] Arthur, N. L., and Bell, T. N., *Rev. Chem. Intermed.*, 1978, **2**, 37.
[5] Arthur, N. L., and Lee, M.-S., *Aust. J. Chem.*, 1976, **29**, 1483.