Hydrogen abstraction from toluene by methyl radicals and the pressure dependence of the recombination of methyl radicals

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Using dimethylzinc, dimethylmercury, and trimethylbismuth as sources of methyl radicals, values of $k_1/k_2^{1/2}$

[1]
$$CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_7H_4$$

[2] $2CH_3 + M \rightarrow C_2H_6 + M$

have been calculated from 338 to 610 °C over the pressure range 4.5-204 mm. M is predominantly toluene. The observed pressure dependence of reaction [2] is in agreement with that found when M = benzene, but is somewhat greater, and the fall-off occurs at higher pressures, than for ethane dissociation. However, reasonable agreement is obtained if it is assumed that the efficiency of toluene as a third body in reaction [2] is about 1/10th that of ethane.

Extrapolation to infinite pressure, where it is assumed that $E_2 = 0$ and $A_2 = 10^{13.34}$ cm³ mole⁻¹ s⁻¹, gives $E_1 = 8.0 \pm 0.3$ kcal mole⁻¹ and $A_1 = 10^{11.07}$ cm³ mole⁻¹ s⁻¹.

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Introduction

Previous investigations of the abstraction of hydrogen from toluene by methyl radicals have given activation energies from 7.3-9.5 kcal mole⁻¹ over the temperature range 100-300 °C (1-5). Previous discrepancies are discussed and the values reported are considered as a possible example of the temperature dependence of Arrhenius parameters.

The pressure dependence of the recombination of methyl radicals and of the dissociation of ethane have been the subject of many investigations. Eleven of these have been discussed in a review article (6). A further study by Trenwith (7) is included in results of the ethane dissociation discussed by Lin and Laidler in a theoretical paper (8). Using the classical Kassel theory, Loucks (9) found a value of s between 8 and 9 best fitted his data for methyl-radical recombination (200-300 °C). Grotewold et al. (10) suggest that the observed pressure dependence of methyl radical recombination indicates a semirigid activated complex and that, as a result, the commonly accepted A factor for this reaction at infinite pressure, 10^{13,34} cm³ mole⁻¹ s⁻¹, is at least an order of magnitude too large. These conclusions are not confirmed by other investigations and

seem unfounded. In particular, the results of Hole and Mulcahy (11) and the discussions of Lin and Laidler (8) indicate a rather loose complex.

Experimental

Materials

(a) Dimethylmercury was prepared by adding methyl magnesium iodide to an ether slurry of mercuric chloride (12).

(b) Dimethylzinc was prepared by refluxing excess zinc metal with dimethylmercury under a nitrogen atmosphere. After refluxing for 12 h, the fraction boiling at 41 °C at 712 mm was removed. The reflux was allowed to continue for an additional 4 h, at which time the fraction boiling at 42 °C at 722 mm was collected. The alkyl was degassed and stored under its own vapor pressure at -78 °C. The dimethylzinc had a vapor pressure of 122 mm at 0 °C, which is in agreement with the literature (13).

(c) Trimethylbismuth was prepared by adding anhydrous bismuth trichloride to methyl magnesium iodide (14). The addition was carried out under a nitrogen atmosphere over a period of 3 h. The mixture was refluxed for an additional 3 h. The excess Grignard was hydrolyzed by pouring the solution over an ice-water mixture containing ammonium chloride. The ether layer was separated, washed three times with distilled water, and dried over sodium sulfate. The ether fraction was removed at reduced pressure and the remaining solution fractionally distilled under a nitrogen atmosphere. The fraction boiling at 52 to 53.5 °C at 120 mm was collected and stored under its own vapor pressure at -78 °C. Small fractions were discarded until the vapor pressure agreed with the literature value of 104 mm at 0 °C (15).

(d) Toluene from sulfonic acid (Eastman Organic X325) was prepared for use by refluxing over sodium under vacuum for 24 h and then degassing twice by bulbto-bulb distillation.

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Apparatus and Procedure

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The experiments were carried out using the same plugflow system previously used in studying the decomposition of dimethylmercury in a benzene carrier (12). The gaseous products which passed a trap at -120 °C were analyzed using a Perkin-Elmer Model 154 gas chromatograph equipped with a 1/4 in. × 6 ft silica gel column. The column was maintained at 80 °C and a helium flow rate of 20 cm³/min was used.

The liquid products which condensed along with the toluene in an acetone – Dry Ice trap were analyzed using a Perkin–Elmer Model 800 gas chromatograph equipped with a 150 ft \times 0.02 in. (inside diameter) Golay column coated with poly(propylene glycol) (isothermal operation at 50 °C; inlet pressure of N₂ carrier, 7 lb).

Results and Discussion

The reactions of methyl radicals generated by the thermal decomposition of metal alkyls in the presence of a large excess of toluene may be represented by the following scheme

$$[1] \qquad CH_3 + C_6H_5CH_3 \rightarrow CH_4 + C_7H_7$$

 $[2] \qquad \qquad 2CH_3 + M \rightarrow C_2H_6 + M$

At the temperatures used in the present work, 338-610 °C, the C_7H_7 formed in reaction [1] is predominantly $C_6H_5CH_2$. The work of Cher *et al.* (5) shows that E_1 and $E_{side \ chain}$ should be virtually identical, while A_1 should be about $10^{0.04}$ greater than $A_{side \ chain}$. Therefore, although the Arrhenius parameters obtained in the present work refer to the overall abstraction process, they should not differ significantly from those associated with abstraction from the side chain of toluene.

The experimental results are given in Table 1, and Arrhenius plots at various fixed pressures are shown in Fig. 1. The observed pressure effect is assumed to arise solely from the third-body requirements of reaction [2]. The infinite-pressure curve was obtained by extrapolation based primarily on the curves for the four highest pressures, using the procedure suggested by Oref and Rabinovitch (16).

The pressure dependence agrees with that observed when M = benzene (17). If it is assumed that the efficiency of benzene and toluene as third bodies in reaction [2] is only about 1/10th that of ethane, then the present results agree very well with those of Trenwith (7), but show a somewhat stronger pressure dependence than suggested by Lin and Laidler (8).

The Arrhenius curves of $k_1/k_2^{1/2}$ at infinite pressure and 4.5 mm may be represented, respectively, by

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Variation of $k_1/k_2^{1/2}$ with temperature and pressure

Radical source	Total pressure mm	Tem- perature °K	$k_1/k_2^{1/2}$	Number of runs averaged*
Zn(CH ₃) ₂	200 200 101 48 48 48 48	857 847 840 883 869 842	308 236 259 385 400 372	3
Hg(CH ₃) ₂	204 204 204 204	777 744 733 714	160 122 121 97	2 2 2
	$ \begin{array}{r} 106 \\ 106 \\ 86 \\ 72 \\ 51 \\ 51 \\ 51 \\ 51 \\ 46 \\ 28 \\ 27 \\ 26 \\ 21 \\ 16 \\ 14 \\ 12 \\ 9.6 \\ 8.2 \\ 7.0 \\ 5.7 \\ 4.5 \\ 7.5 \\ 4.5 \\ 7.5 \\ 4.5 \\ 7.$	744 733 714 731 715 781 769 756 714 798 799 798 798 799 798 799 799 798 799 799	132 141 99 128 116 219 129 125 335 321 322 365 381 157 443 444 181 473 501 950 846 752	2 2 4 2 2
	4.5 4.5 4.5 4.5	813 800 787 772	656 570 516 424	7 4 6 2
Bi(CH₃)₃	204 204 106 106 86 51 51 51	649 629 630 611 628 631 626 622	54 51 36 50 49 48 48	2 2 4
	24 24 4.5 4.5 4.5 4.5 4.5	693 683 672 703 694 685 676 659	114 113 88 184 168 158 148 105	2 2 2 2 8 2

*Number of runs averaged to obtain the given value of $k_1/k_2^{1/2}$. Variation in individual runs $< \pm 10\%$ in the value of $k_1/k_2^{1/2}$.

$$(k_1/k_2^{1/2})_{\infty} = 2.5 \times 10^4 \exp(-8000 \pm 300/RT) \text{ mole}^{-1/2} (\text{cm}^3)^{1/2} \text{ s}^{-1/2}$$

and

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$(k_1/k_2^{1/2})_{4.5} = 1 \times 10^6 \exp(-11\ 900 \pm 300/RT) \text{ mole}^{-1/2} (\text{cm}^3)^{1/2} \text{ s}^{-1/2}$

If E_1 is independent of pressure, then E_2 at 4.5 mm is -7.8 kcal mole⁻¹. This is consistent with the results of Hole and Mulcahy (11) who estimate that in the third-order region $E_2 = -13$ kcal mole⁻¹.

In Fig. 2, the present results are compared with previous studies of reaction [1]. The work of Trotman-Dickenson and Steacie (1) agrees quite well with that of Mulcahy *et al.* (4) and of Cher *et al.* (5), but has been omitted because of the uncertainty in correction for isotopic impurity. The latter two studies give $E_1 = 9.2$ and 9.5 kcal mole⁻¹, respectively. Over their concurrent temperature range, these two studies can be adequately represented by a single curve, the solid portion for curve 2 in Fig. 2. This may be somewhat fortuitous since the results of Mulcahy *et al.* may be in a pressure dependent region and should



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FIG. 1. Arrhenius plot of $k_1/k_2^{1/2}$ at various pressures. Numbers beside the points indicate number of runs averaged to obtain the point. Full points are from curves of $k_1/k_2^{1/2}$ vs. pressure and are usually coincident with experimental points. Pressure: \bigcirc , 4.5; \triangle , 24; \bigcirc , 50; \bigtriangledown , \bigcirc , 106; \bigcirc , 204 mm; 1 = infinite pressure; length of bar indicates estimated uncertainty in the extrapolated value.



FIG. 2. Arrhenius plots of abstraction of hydrogen from toluene by methyl radicals. All values based on $k_2 = 10^{13.34}$ mole⁻¹ cm³ s⁻¹. *I*, this work, bars indicate estimated uncertainty; 2, composite of results of Cher, Hollingsworth, and Sicilio (5) and of Mulcahy, Williams, and Wilmshurst (4); dashed curve indicates the additional temperature range covered by Cher *et al* (5); 3, Burkley and Rebbert (3); 4, Rebbert and Steacie (2).

probably be decreased by about 0.1 log units, putting them more in line with those of Burkley and Rebbert (3) (curve 3, Fig. 2).

The present results are basically in agreement with previous investigations, although the activation energy obtained is 1.2–1.5 kcal below the most recent results at lower temperatures (4, 5). At least part of this difference may be real. Marshall and Purnell (18) predict a minimum temperature dependence of $T^{-1/2}$ for the activation energy of the abstraction reaction. This leads to an expected minimum difference of 0.3 kcal, compared to the experimental difference of 1.4 \pm 0.6 kcal. Whether the actual temperature dependence could explain the complete difference is uncertain.

The calculations of Marshall and Purnell also indicate that the A factor for reaction [2] at infinite pressure should decrease by at least 0.15

log units from room temperature to 475 °K and then should show little variation from this temperature up to at least 900 °K. It is possible, therefore, that all the curves shown in Fig. 2 should be lowered by at least 0.08 log units. This effect would also explain at least a significant part of the curvature in the Arrhenius plot of $k_1/k_2^{1/2}$ observed by Cher et al. (5) below approximately 425 °K.

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