1008. *Kinetics of Free-radical Reactions in Solution. Part II.*[1] *The Reaction of Benzyl Radicals with Substituted Toluenes.*

By R. A. JACKSON.

The abstraction of hydrogen atoms from the α-position of various substituted toluenes by benzyl radicals in the liquid phase has been studied. In the case of *p*-chlorotoluene, the Arrhenius parameters for the reaction have been determined.

THE transfer reactions of benzyl radicals with substituted toluenes are of interest, because quantitative data for these reactions are scanty and there is some doubt whether such reactions occur in solution to an appreciable extent.[2]

To obtain more information, dibenzylmercury (a thermal source of benzyl radicals [3,4]) was added slowly to boiling *p*-chlorotoluene. When all the dibenzylmercury had been

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[1] Part I, preceding paper.

[2] Brown and Russell, *J. Amer. Chem. Soc.*, 1952, **74**, 3995; Wang and Cohen, *ibid.*, 1957, **79**, 1924; Eliel, Wilken, Fang, and Wilen, *ibid.*, 1958, **80**, 3303; Cadogan, Gold, and Satchell, *J.*, 1955, 561.

[3] Horrex, personal communication.

[4] Razuvaev and Koton, *Ber.*, 1932, **65**, 613; Koton, *Doklady Akad. Nauk S.S.S.R.*, 1953, **88**, 991.

decomposed, analysis of the products showed the presence of mercury, bibenzyl, 4-chlorobibenzyl, and 4,4′-dichlorobibenzyl.

This suggests that in the reaction scheme

$$\mathrm{Hg(CH_2Ph)_2} \longrightarrow \mathrm{Hg} + 2{\bullet}\mathrm{CH_2Ph} \quad \ldots \ldots \quad (1)$$

$$2{\bullet}\mathrm{CH_2Ph} \longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}CH_2Ph} \quad \ldots \ldots \quad (2)$$

$$\mathrm{Ph{\cdot}CH_2{\bullet}} + \mathrm{CH_3{\cdot}C_6H_4Cl} \longrightarrow \mathrm{Ph{\cdot}CH_3} + {\bullet}\mathrm{CH_2{\cdot}C_6H_4Cl} \quad \ldots \ldots \quad (3)$$

$$\mathrm{Ph{\cdot}CH_2{\bullet}} + {\cdot}\mathrm{CH_2{\cdot}C_6H_4Cl} \longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4Cl} \quad \ldots \ldots \quad (4)$$

$$2{\bullet}\mathrm{CH_2{\cdot}C_6H_4Cl} \longrightarrow \mathrm{Cl{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4Cl} \quad \ldots \ldots \quad (5)$$

reaction (3) takes place to a considerable extent, giving rise to 4-chlorobenzyl radicals, which subsequently dimerize or react with benzyl radicals to give the chlorinated bibenzyls observed.

It was hoped that by addition of dibenzylmercury at a constant rate to *p*-chlorotoluene at constant temperature, a steady-state system with a constant concentration of benzyl radicals would be set up, and that this would allow information about the rate constant for reaction (3) to be deduced from the proportions of the various products formed. The difficulties of slow, constant-rate addition, evaporation of liquid, and exclusion of oxygen proved to be too great, and a new technique was devised. Solutions of dibenzylmercury in *p*-chlorotoluene were degassed, sealed under a vacuum, and heated in an oil-thermostat-bath until all the dibenzylmercury had decomposed (20 half-lives). The bibenzyls produced (which accounted for more than 91% of the dibenzylmercury) were analysed quantitatively by gas chromatography. From the relative proportions of the bibenzyls it is possible[1] to calculate a composite rate constant $K = k_3/(k_1k_2)^{\frac{1}{2}}$ in spite of the fact that the radical concentrations are falling throughout the reaction, provided that benzyl and 4-chlorobenzyl radicals recombine at the statistical rate, *i.e.*, $k_2 : k_4 : k_5 = 1 : 2 : 1$. This was shown to be the case by a separate experiment where t-butyl peroxide was decomposed in toluene-*p*-chlorotoluene mixtures. The reactive t-butoxy-radicals, with the toluenes, gave a mixture of benzyl and 4-chlorobenzyl radicals. The amounts of the various bibenzyls produced were in accordance with the statistical recombination rates.

From a knowledge of K, the rate constant for the transfer reaction, k_3, can be evaluated since both k_1 and k_2 are known.[3,5] By performing experiments at different temperatures in the range 140—170°, the Arrhenius parameters for the transfer reaction (3) were deduced to be $\log_{10} A_3 = 9{\cdot}88$, $E_3 = 20{\cdot}3$ kcal./mole. The activation energy is probably more reliable than the pre-exponential factor because of the uncertainty[5] in the absolute value of k_2.

Radical-transfer reactions are of first order with respect to radical concentration and usually involve appreciable activation energies; recombination reactions are of second order with respect to radical concentrations and have zero or very small activation energies. Thus, if the high activation energy observed for the reaction of benzyl radicals with *p*-chlorotoluene is typical for reactions of benzyl radicals with toluenes in solution, we may expect such reactions to be unimportant except at high temperatures or in very dilute solutions. This accords with most of the qualitative results available.[2]

Thermoneutral transfer reactions of simple alkyl radicals have activation energies in the region of 14 kcal./mole.[6] The greater activation energies involved in transfer reactions of benzyl radicals probably reflect a loss of resonance energy in the transition state, though speculation on this matter is likely to be unprofitable until more experimental results are available.

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[5] MacCarthy and McLachlan, *Trans. Faraday Soc.*, 1960, **56**, 1187.

[6] Boddy and Steacie, *Canad. J. Chem.*, 1960, **38**, 1576.

Other Substituted Toluenes.—The reactions of benzyl radicals with ethylbenzene, isopropylbenzene, and t-butylbenzene were also studied by the same technique. Ethylbenzene appeared to give three main products, but they were not sufficiently well resolved by the gas-chromatography apparatus available for quantitative analysis to be made. Isopropylbenzene gave three well-resolved peaks, identified by their retention times as due to bibenzyl and αα-dimethyl- and αα′α′-tetramethyl-bibenzyl. Unfortunately, the recombination rates of benzyl and αα-dimethylbenzyl radicals are not in the statistical proportions, probably because of the steric effect of the two methyl groups. Thus the rate constant for the transfer reaction could not be worked out as in the case of *p*-chlorotoluene. However, the variation of proportions of products with temperature was similar to that shown by *p*-chlorotoluene, so that the activation energy is probably the same within a few kilocalories.

t-Butylbenzene did not react with benzyl radicals under the conditions used. t-Butylbenzene contains no α-hydrogen atom, and of the other possible transfer reactions

$$\mathrm{Ph{\cdot}CH_2{\bullet} + Ph{\cdot}CMe_3 \longrightarrow Ph{\cdot}CH_3 + Ph{\cdot}CMe_2{\cdot}CH_2{\bullet}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

$$\mathrm{Ph{\cdot}CH_2{\bullet} + Ph{\cdot}CMe_3 \longrightarrow Ph{\cdot}CH_2{\cdot}CH_3 + Ph{\cdot}CMe_2{\bullet}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

reaction (6) will be very unfavourable energetically, whilst (7), though probably favourable thermodynamically, requires the transfer of a methyl group rather than of a single hydrogen atom. Such processes rarely occur, and must be presumed to have high activation energies.[7]

EXPERIMENTAL

Gas Chromatography.—" Embaphase " silicone oil, supported on kieselguhr was used as the stationary phase. Column temperatures of 180—200° were employed.

Solvents were purified by fractional distillation. Cumene was purified by Vogel's method.[8] Dibenzylmercury,[9] 4-chlorobibenzyl,[10] 4,4′-dichlorobibenzyl,[11] and bicumyl [12] were made by established methods.

Bibenzyl.—A solution of t-butyl peroxide (10 ml.) in toluene (500 ml.) was refluxed for 4½ days. The solvent was removed by fractional distillation at atmospheric pressure, and the yellow oil remaining was distilled at 8 mm. Bibenzyl (5·2 g.) was collected at 135° and, recrystallized from methanol, had m. p. 53—53½° (lit., 52°).

αα-Dimethylbibenzyl.[13]—This was made by Friedel–Crafts reaction of 1,2-dibromo-2-methylpropane with benzene. The product, described in the literature as a fluorescent liquid, b. p. 284—287°, was collected between these temperatures, but solidified in the collecting flask and, recrystallized from methanol, had m. p. 128—129° (Found: C, 91·1; H, 8·7. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%).

Decomposition of Dibenzylmercury in p-*Chlorotoluene.*—Solutions of dibenzylmercury (0·100 g.) in *p*-chlorotoluene (25 ml.) were introduced into Pyrex ampoules, degassed, sealed under a vacuum and heated at temperatures of 140—170° in an oil thermostat-bath until all the dibenzylmercury had decomposed (20 half-lives). The organic products were identified as bibenzyl, 4-chlorobibenzyl, and 4,4′-dichlorobibenzyl by their gas-chromatographic retention times and were analysed quantitatively by comparison with authentic mixtures. The results (average of two determinations at each temperature) are shown in Table 1.

Values of $K = k_3/(k_1k_2)^{\frac{1}{2}}$ were worked out as described in Part I.[1] The Arrhenius parameters for the composite rate constant K were evaluated as $\log_{10} A = \bar{3}{\cdot}952$, $E = 0{\cdot}91$ kcal./mole.

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[7] Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955, p. 238.

[8] Vogel, *J.*, 1948, 607.

[9] Banus, *Anales Soc. españ. Fís. Quím*, 1922, **20**, 667.

[10] Bergmann, Weizman, and Schapiro, *J. Org. Chem.*, 1944, **9**, 408.

[11] Beckwith and Waters, *J.*, 1957, 1665.

[12] Kharasch, McBay, and Urry, *J. Org. Chem.*, 1945, **10**, 401.

[13] Bodroux, *Compt. rend.*, 1901, **132**, 1335.

Since the Arrhenius parameters for reactions (1) and (2) are known [3,5] [$\log_{10} A_1 = 16{\cdot}25$, $E_1 = 38{\cdot}8$ kcal./mole; $\log_{10} A_2 = 7{\cdot}60$, $E_2 = 0$], those for the transfer reaction (3) were derived as $\log_{10} A_3 = 9{\cdot}88$, $E_3 = 20{\cdot}3$ kcal./mole.

TABLE 1.

Temp.	Bibenzyl (mole %)	4-Chlorobibenzyl (mole %)	4,4′-Dichlorobibenzyl (mole %)	K
139·7°	77·6	19·1	3·33	0·00293
156·1	75·8	20·6	3·65	0·00309
171·4	73·1	23·0	3·96	0·00318

Radical Balance.—Use of carbazole as an external standard during gas chromatography of the products of the reaction of dibenzylmercury with *p*-chlorotoluene showed that the various bibenzyls produced accounted for more than 91% of the dibenzylmercury.

Cage Recombination.—The percentage of bibenzyl formed in the above reactions was in all cases greater than that expected from the proportions of the substituted bibenzyls. This excess is attributed to recombination of benzyl radicals within a solvent cage, or possibly to the decomposition of part of the dibenzylmercury by a molecular mechanism. The percentage of radicals lost in this way was estimated as 40% at 140°, dropping to 27% at 171°.

Reaction of t-Butyl Peroxide with Mixtures of Toluene and p-*Chlorotoluene.*—Mixtures of toluene, *p*-chlorotoluene, and t-butyl peroxide [(*a*) 4 : 2 : 1; (*b*) 3 : 3 : 1; (*c*) 2 : 4 : 1 v/v] were sealed in ampoules and heated at 108·7° for 77 hr. The products were analysed quantitatively as after the reaction of dibenzylmercury with *p*-chlorotoluene, and consisted of a mixture of the same bibenzyls.

TABLE 2.

Solution	[BB]/[BC]	[CC]/[BC]	Selectivity	k_2/k_4	k_5/k_4
(*a*)	1·137	0·263	0·96	0·511	0·586
(*b*)	0·562	0·395	1·07	0·505	0·440
(*c*)	0·301	0·843	1·07	0·541	0·469
		Average	1·03	0·519	0·498

B = Benzyl; C = 4-Chlorobenzyl.

Selectivity in column (4) is defined as

$$\frac{\{2\,[\mathrm{BB}] + [\mathrm{BC}]\}/[\mathrm{BH}]}{\{2\,[\mathrm{CC}] + [\mathrm{BC}]\}/[\mathrm{CH}]},$$

i.e., the ratio of benzyl to 4-chlorobenzyl radicals present in the products, divided by the ratio of concentrations of toluene to *p*-chlorotoluene. The value unity found implies that t-butoxy-radicals do not discriminate between toluene and *p*-chlorotoluene in abstraction of hydrogen. Columns (5) and (6) are calculated from the ratios $\frac{[\mathrm{BB}]/[\mathrm{BH}]}{[\mathrm{BC}]/[\mathrm{CH}]}$ and $\frac{[\mathrm{CC}]/[\mathrm{CH}]}{[\mathrm{BC}]/[\mathrm{BH}]}$, respectively. The means of these ratios give $k_2 : k_4 : k_5 = 0{\cdot}52 : 1 : 0{\cdot}50$ or 1 : 2 : 1 within the limits of experimental error.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, LEICESTER. [*Received, April* 17*th*, 1963.]