[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Kinetics of the Reaction of Tri-*p*-biphenylmethyl and of tri-*p*-*t*-butylphenylmethyl with Toluene

BY R. M. DOBRES AND P. W. SELWOOD

A recent communication[1] from this Laboratory has described certain results of a magnetic study on toluene solutions of hexa-*p*-biphenylethane and of hexa-*p*-*t*-butylphenylethane. Mention was made of the fact that at moderately elevated temperatures the magnetic susceptibilities of both systems decrease with time, indicating gradual disappearance of the free radicals. The purpose of the work described here was to establish the nature of this process.

Experimental

Preparation and analysis of ethane solutions and determination of magnetic susceptibilities have been described previously.[1]

Isolation of Products from the Reaction of Hexa-*p*-biphenylethane with Toluene.—The starting material in a preliminary experiment was the contents of the magnetic sample tube after three runs, together with an equal volume of solution heated at 140° in a sealed vessel in the dark until all color indicative of free radical had disappeared. All of the material had been prepared and handled in closed systems, previously evacuated and protected from exposure to light.

The toluene was distilled at room temperature, leaving a yellow-colored residue. This was taken up in toluene, brought into solution at reflux and allowed to crystallize. The white crystals (I) which separated were recrystallized from toluene, washed with alcohol and dried, m.p. 230–231.5°, cor. The filtrate from the crystallization was evaporated to dryness. The brown residue was recrystallized from amyl acetate, yielding white crystals (II) which were washed with alcohol and dried, m.p. 193–197°, cor.

In another experiment, 0.73 g. of tri-*p*-biphenylmethylchloride in 85 ml. of toluene was stirred with 2.35 g. of "molecular" silver in the same evacuated system previously described for preparing the radical solution. The vessel containing the filtered solution was sealed, then heated at 140° in the dark until the deep burgundy color of the radical had given way to a light yellow-colored solution. This solution was maintained at −10° overnight, whereupon the white crystals (I) which formed were filtered off, washed with ether and dried *in vacuo;* yield 0.32 g., m.p. 231–232°, cor.[2]

Anal. Calcd. for tri-*p*-biphenylmethane, $C_{37}H_{28}$: C, 94.03; H, 5.97; mol. wt., 472. Found: C, 94.07; H, 6.00; mol. wt., 481.

The filtrate from the crystallization of I was concentrated to 15 ml., heated to complete solution at reflux and allowed to crystallize at −10°. An additional 0.06 g. of I was obtained. The pale yellow filtrate was evaporated on the steam-bath, leaving a light brown residue. This was extracted successively with three portions of ether after which there remained 0.08 g. of white crystals (II), m.p. 194–195.5°, cor. The three ether extracts were evaporated to dryness. The first gave 0.08 g. of light brown material which yielded more of I and II when fractionally crystallized from alcohol–benzene. The second and third had melting points of 194–195.5° and 195–196°, cor., respectively. Their combined weight was 0.14 g. The white crystals of II from these various fractions were combined, recrystallized from alcohol–benzene and dried *in vacuo*, m.p. 194–195°, cor.

Anal. Calcd. for tri-*p*-biphenylbenzylmethane, $C_{44}H_{44}$: C, 93.91; H, 6.09; mol. wt., 563. Found: C, 93.80; H, 6.13; mol. wt., 561.

The combined amount of I and II recovered was somewhat over 90% of that calculated on the basis of a 90% conversion of the methyl chloride to radical and a quantitative reaction of radical with solvent. It was assumed, then, that no appreciable amount of an undetected third product was formed.

The quantitative nature of the reaction between radical and solvent was demonstrated by the following experiment. The weight fraction of total solute was determined on two portions of the same radical solution; one as prepared, the other after heating at 140° until reaction was complete, indicated by the absence of radical color. Again exposure to air or light was excluded. The weight fraction of solute in the first solution was 0.0135 ± 0.0001; that in the second, 0.0146 ± 0.0001. For a quantitative reaction with toluene, 0.0135 g. of solute, 93.5% of which analyzed indirectly for ethane, would have produced 0.0147 g. of solid product. The reaction is therefore quantitative within the limits of experimental error.

Molecular weights were measured by an improved Rast camphor method.[3] The accuracy is believed to be within a few per cent., based on the results obtained with several known compounds.

Results and Discussion

The experimental evidence which served as a basis for the mechanism proposed for the reaction of tri-*p*-biphenylmethyl with toluene was the following: (1) The magnetic susceptibility of the solution decreased with measurable velocities above 50°. (2) Two products were isolated from the reaction mixture in high yield. One is tri-*p*-biphenylmethane. The other is tentatively identified as tri-*p*-biphenylbenzylmethane. (3) The reaction between radical and solvent is quantitative A three-stage reaction process is postulated

(a) $$\mathrm{R{-}R} \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2\mathrm{R}\cdot$$

(b) $$\mathrm{R}\cdot + \mathrm{H{-}S} \xrightarrow{k_3} \mathrm{R{-}H} + \mathrm{S}\cdot$$

(c) $$\mathrm{R}\cdot + \mathrm{S}\cdot \xrightarrow{k_4} \mathrm{R{-}S}$$

where

R–R is undissociated ethane
R· is the corresponding free methyl radical
H–S is toluene
S· is a free radical derived from toluene, presumably the benzyl radical
R–S is a compound produced by electron pairing of R· + S·

Since the susceptibility decreases relatively slowly with time, the triarylmethyl radicals are considered to be in equilibrium with the parent ethane. It is also assumed that the solvent free-radicals can be represented in a steady-state concentration. It then follows that

$$-\mathrm{d}[\mathrm{R}\cdot]/\mathrm{d}t = 2k_3[\mathrm{R}\cdot][\mathrm{H{-}S}] \qquad (1)$$

Toluene was always in excess of 99.8 mole % so that

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[1] Selwood and Dobres, THIS JOURNAL, **72**, 3860 (1950).

[2] *Beilstein*, 1st Supplement, Vol. 5, p. 391, gives for the methane when crystallized from benzene, 231–232°; the 2nd Supplement, Vol. 5, p. 717, lists 233°.

[3] R. M. Dobres, Ph.D. Thesis, Northwestern University, 1949.

its concentration is considered essentially constant. We set

$$k = 2k_3[\text{H–S}] \quad (2)$$

so that

$$-\text{d}[\text{R}\cdot]/\text{d}t = k[\text{R}\cdot] \quad (3)$$

and

$$k = \frac{1}{t} \ln \frac{[\text{R}\cdot]_0}{[\text{R}\cdot]_t} \quad (4)$$

The concentration of triarylmethyl is proportional at any time to the product $[\text{M}\alpha]_t$ where M is ethane concentration in moles per unit volume and α is degree of dissociation. Therefore

$$k = \frac{1}{t} \ln \frac{[\text{M}\alpha]_0}{[\text{M}\alpha]_t} \quad (5)$$

The concentration of ethane decreases with time so that $[\text{M}]_t$ is not known directly. We define, therefore, an apparent degree of dissociation, $\alpha_{\text{app(t)}}$, which multiplied by the initial concentration of ethane gives a quantity proportional to $[\text{R}\cdot]_t$. By definition

$$\alpha_{\text{app(t)}} = [\text{M}\alpha]_t / [\text{M}]_0 \quad (6)$$

so that

$$k = \frac{1}{t} \ln \frac{\alpha_0}{\alpha_{\text{app(t)}}} \quad (7)$$

The apparent degree of dissociation is calculated in the usual way, treating the initial concentrations of reactants as constants.

TABLE I

KINETICS OF THE REACTION OF TRI-*p*-BIPHENYLMETHYL WITH TOLUENE

Temp., °C.	Init. molal concn. of ethane	Time, hr.	$-\chi$ solution $\times 10^6$	$\alpha_{\text{app.}}$	k, hr.$^{-1}$
70	0.0162	0	0.6803	0.758	. . .
		2	.6810	.737	0.014
		4.5	.6821	.709	.015
		11.5	.6841	.647	.014
		17	.6858	.598	.014
		23.5	.6876	.546	.014
		44	.6927	.398	.015
		64	.6967	.281	.015
				Av. k	0.0145
76	0.0095	0	0.6936	0.672	. . .
		6	.6956	.572	0.027
		13	.6974	.484	.025
		25	.6994	.385	.022
		36	.7010	.306	.022
		50	.7025	.233	.021
		64	.7036	.178	.021
		84	.7050	.109	.022
				Av. k	0.023
90	0.0134	0	0.6893	0.657	. . .
		1.25	.6913	.586	0.091
		3.75	.6943	.478	.085
		6.25	.6966	.395	.081
		8.75	.6984	.331	.078
		11.25	.7001	.271	.079
		13.75	.7014	.223	.079
		21.25	.7045	.112	.083
				Av. k	0.082

TABLE II

KINETICS OF THE REACTION OF TRI-*p*-*t*-BUTYLPHENYLMETHYL WITH TOLUENE

Temp., °C.	Init. molal concn. of ethane	Time, hr.	$-\chi$ solution $\times 10^6$	$\alpha_{\text{app.}}$	k, hr.$^{-1}$
50	0.0048	0	0.6944	0.578	. . . .
		10	.6948	.559	0.0033
		20	.6952	.541	.0033
		30	.6955	.526	.0031
		40	.6960	.503	.0035
				Av. k	0.0033
60	0.0052	0	0.6993	0.686	. . . .
		5	.6998	.639	0.014
		10	.7002	.603	.013
		15	.7006	.566	.013
		20	.7010	.529	.013
		30	.7016	.474	.012
		40	.7022	.418	.012
		50	.7025	.390	.011
		60	.7028	.363	.011
		70	.7030	.344	.010
				Av. k	0.012
80	0.0091	0	0.7022	.496	. . . .
		2.5	.7030	.424	.063
		5	.7037	.362	.063
		7.5	.7043	.309	.063
		10	.7047	.273	.060
		15	.7056	.193	.063
				Av. k	0.063

The kinetic data for the reaction of tri-*p*-triphenylmethyl with toluene in three experiments are given in Table I; those for tri-*p*-*t*-butylphenylmethyl are listed in Table II. It was assumed that the same mechanism operated in both cases, although no attempt was made to isolate the products of the reaction of tri-*p*-*t*-butylphenylmethyl. The justification for this assumption was the structural similarity of the two radicals with respect to the absence of hydrogen on the carbons alpha to the aromatic rings joining the methyl carbon. This structural feature, as well as the kinetic data, rules out the possibility of a bimolecular disproportionation reaction between two molecules of radical to produce a paraffin and an olefin or its polymer.[4,5] The kinetic data also rule out the possibility of an irreversible dimerization. In particular, the reasonably constant value for the rate constant in all experiments with each radical is consistent only with the postulate of a pseudo first order reaction between radical and solvent. The activation energy for the process involving toluene has been calculated as 22 kcal./mole for tri-*p*-biphenylmethyl and 21 kcal./mole for tri-*p*-*t*-butylphenylmethyl. Taking

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[4] Marvel, Rieger and Mueller, THIS JOURNAL, **61**, 2769 (1939). Marvel, Mueller, Himel and Kaplan, *ibid.*, **61**, 2771 (1939).

[5] Selwood and Preckel, *ibid.*, **65**, 895 (1943).

this value, together with the data in Table I at 70°, the pre-exponential component of the bimolecular rate constant, k_3, is calculated as 2×10^{10} cc. mole^{-1} sec.$^{-1}$. This leads, assuming a collision cross section of 10^{-7} cm., to a steric factor of 4×10^{-5}. This is in agreement with the rather low steric factors that have recently been postulated for the hydrogen abstraction reactions of unsubstituted methyl radicals by Steacie, Darwent and Trost,[6] and by Dorfman and Gomer.[7] The graphs of the data which yielded the activation energies are illustrated in Figs. 1 and 2. The accuracy is believed to be ~10%.

The reaction between radical and solvent described in this work is related to the phenomenon of chain transfer during the polymerization of styrene in the presence of solvent.[8] In the chain transfer step a growing polymer radical abstracts an atom from the solvent to produce a solvent free radical and a completed polymer molecule. The extent to which different solvents are capable of transferring an atom has been estimated from the degree of polymerization, so that by molecular weight studies it has been possible to evaluate "chain-transfer constants" which measure the relative reactivity of various solvents. It is now possible to suggest alternative and perhaps simpler methods for obtaining these data. The rate at which tri-p-biphenylmethyl reacts with different solvents can be determined either magnetically or spectrophotometrically, since the decrease in radical concentration appears to be paralleled by a decrease in intensity of color.

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Summary

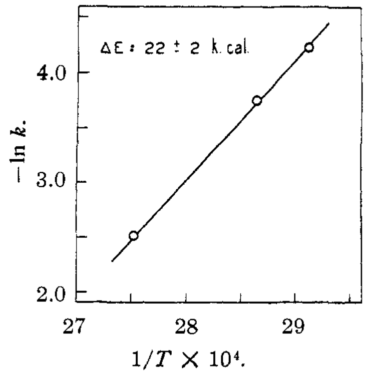

Fig. 1.—ln k vs. $1/T$ for the reaction of tri-p-biphenylmethyl with toluene.

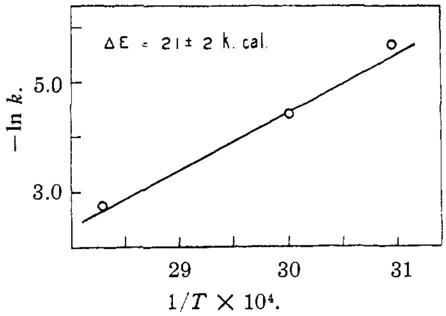

Fig. 2.—ln k vs. $1/T$ for the reaction of tri-p-t-butylphenylmethyl with toluene.

Evidence is presented for the mechanism of the reactions of hexa-p-biphenylethane and of hexa-p-t-butylphenylethane, *via* their corresponding free radicals, with toluene. The reaction is quantitative and first order with respect to triarylmethyl radical, with activation energies of 22 and 21 kcal./mole, respectively. A new method is proposed for comparing the chain transfer activity of various solvents in free radical reactions.

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(6) Steacie, Darwent and Trost, "The Labile Molecule," Discussions, *Faraday Soc.*, No. 2, 1947, p. 80.

(7) Dorfman and Gomer, *Science*, **110**, 439 (1949).

(8) Mayo in Twiss "Advancing Fronts in Chemistry," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1945, p. 47.