KINETICS OF THE REACTION OF REDUCTION OF TRIPHENYLCARBINOL BY ISOPROPYL ALCOHOL IN AQUEOUS SULFURIC ACID MEDIUM BY HYDRIDE TRANSFER

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Abstract

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S. G. ENTELIS, G. V. EPPLE, and N. M. CHIRKOV

KINETICS OF THE REACTION OF REDUCTION OF TRIPHENYLCARBINOL BY ISOPROPYL ALCOHOL IN AQUEOUS SULFURIC ACID MEDIUM BY HYDRIDE TRANSFER

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Although the existence of reactions proceeding by transfer of the hydride ion (H^-) had long been assumed, the study of their kinetics and mechanism began only recently ($^{1-4}$). Reactions proceeding through transfer of H^- include, in particular, Meerwein-Ponndorf reactions, for example the reduction of arylcarbinols by aliphatic alcohols in an acidic medium.

In the present work we have studied in detail the kinetics of the reduction of triphenylcarbinol (TPC) to triphenylmethane by isopropyl alcohol in aqueous sulfuric acid over a broad range of concentrations (H_2SO_4 from 45 to 75%; TPC from $4 \cdot 10^{-7}$ to $4 \cdot 10^{-6}$ mole/liter; iso-C_3H_7OH from 0.2 to 1.5 mole/liter) and temperatures (from 35 to 60°).

A preliminary investigation of this reaction was carried out by Bartlett and Kollum (^{2}), who concluded that transfer of the H^- ion occurs from the molecule of isopropyl alcohol to the triphenylmethylcarbonium ion according to the scheme

$$\mathrm{Ph_3C^+ + H : C(CH_3)_2OH \xrightarrow{k_0} Ph_3CH + C^+(CH_3)_2OH} \qquad (1)$$

Since the arylmethyl cation of TPC is formed upon protonation of TPC according to the equation

$$\mathrm{Ph_3COH + H^+ \underset{\leftarrow}{\overset{K_{ArCOH}}{\rightleftarrows}} Ph_3C^+ + H_2O}, \qquad (2)$$

the total concentration of TPC in the reaction mixture $[\mathrm{Ph_3COH}]_0$ is equal to the sum of the concentrations of the ion $[\mathrm{Ph_3C^+}]$ and of the nonionized form of the carbinol $[\mathrm{Ph_3COH}]$:

$$[\mathrm{Ph_3COH}]_0 = [\mathrm{Ph_3C^+}] + [\mathrm{Ph_3COH}]. \qquad (3)$$

On the basis of scheme (1), equations (2), (3), and the equation for the protonation reaction of iso-C_3H_7OH

$$\text{iso-}C_3H_7OH + H^+ \underset{\leftarrow}{\overset{K_{ROH}}{\rightleftarrows}} \text{iso-}C_3H_7OH_2^+ \tag{4}$$

it is not difficult to show that the expression for the rate of disappearance of $[Ph_3C^+]$ in the presence of an excess of alcohol will have the form

$$-d[Ph_3C^+]/dt = k_{eff}[Ph_3C^+], \tag{5}$$

where the effective rate constant observed experimentally is

$$k_{eff} = k_0 \frac{K_{ArCOH}c_0}{1 + K_{ArCOH}c_0} \frac{1}{1 + K_{ROH}h_0} C_{sp}. \tag{6}$$

In equation (6): k_0 is the true rate constant of the limiting step (1); K_{ArCOH} is the equilibrium constant of reaction (2); K_{ROH} is the equilibrium constant of reaction (4); C_{sp} is the total concentration of [iso-C_3H_7OH] in solution; h_0 and c_0 are the negative antilogarithms of the acidity functions of Hammett and Deno, respectively (^{5,6}). The values of the effective constants

rate constants of the reaction were found graphically from the slope of semilogarithmic anamorphoses of the kinetic curves for the decrease in the optical density of the solution at $\lambda = 432$ mμ. The decrease in optical density in accordance with equation (5) imitates a first-order reaction. It reflects the fall in the concentration of the triphenylmethylcarbonium ion, which has an absorption band with $\lambda_{max} = 432$ mμ.

Table 1

[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		58.60% H_2SO_4	
$k_{eff} \cdot 10^2$, min^{-1}	C_{sp}, mol/l	$k_{eff} \cdot 10^2$, min^{-1}	C_{sp}, mol/l	$k_{eff} \cdot 10^2$, min^{-1}	C_{sp}, mol/l	$k_{eff} \cdot 10^2$, min^{-1}	C_{sp}, mol/l	$k_{eff} \cdot 10^2$, min^{-1}	C_{sp}, mol/l	$k_{eff} \cdot 10^2$, min^{-1}	C_{sp}, mol/l	$k_{eff} \cdot 10^2$, min^{-1}	C_{sp}, mol/l
0.40	0.39	1.56	0.16	1.51	0.13	1.10	0.10	0.97	0.10	1.48	0.16	0.94	0.19
0.45	0.43	3.28	0.32	1.74	0.16	2.25	0.20	1.62	0.14	4.91	0.30	2.36	0.45
1.24	1.06	3.78	0.43	2.53	0.21	2.48	0.21	1.49	0.14	3.52	0.38	4.86	0.80
[illegible] H_2SO_4		4.80	[illegible]	[illegible]	[illegible]	2.92	0.25	2.07	0.19	5.46	0.48	60.70% H_2SO_4	
2.10	0.29	4.95	0.69	4.92	0.33	2.92	0.26	2.60	0.26	55.70% H_2SO_4		0.56	[illegible]
2.59	0.43	5.50	0.71	5.16	0.43	3.26	0.28	4.37	0.40	1.68	0.21	1.99	0.50

[illegible] 58.60% H_2SO_4}													
2.92	0.44	[illegible]% H_2SO_4	5.26	0.42	5.59	0.31	4.74	0.45	3.62	0.50	2.46	0.59	
[illegible]% H_2SO_4	3.70	0.31	5.70	0.74	7.41	0.59	5.03	0.45	4.33	0.67	64.80% H_2SO_4		
2.12	0.29	4.01	0.36	6.04	0.48	9.56	0.75	5.01	0.47	8.70	0.81	0.21	0.50
3.74	0.48	4.44	0.46	6.19	0.48	10.3	0.76	5.06	0.48	9.62	0.90	67.0% H_2SO_4	
		5.86	0.68	6.21	0.51	20.9	1.38	5.77	0.50			0	0.5
				7.17	0.53	52.45% H_2SO_4	7.60	0.72			70.0% H_2SO_4		
				8.11	0.60	4.61	0.34	6.75	0.83			0	0.5
				8.15	0.65	4.70	0.40					75% H_2SO_4	
				9.80	0.72	5.60	0.44					0	0.5
				4.04	0.97	6.91	0.58						
				15.00	1.99								

Observation of the course of the transformation was carried out on a recording double-beam spectrophotometer of the SF-2M type, equipped with a device for recording kinetics. The reaction was conducted directly in all-glass cuvettes 5 cm long, placed in a thermostated cuvette holder. The temperature in the cuvettes was maintained with an accuracy of ±0.5°.

In Table 1, as an example, the values obtained for k_{eff} at $T = 40°$ are given for various C_{sp} and sulfuric acid concentrations. Figure 1 presents the dependence of k_{eff} on the initial concentration of H_2SO_4 at $C_{\text{sp}} = 0.5$ mol/l. It is seen that the reaction under study proceeds in a narrow concentration region bounded by bell-shaped curves, the maximum of which, independently of temperature, lies approximately at 50.5% H_2SO_4. This form of the curves is a consequence of the fact that in the limiting stage (1) an ion participates whose concentration increases with acid concentration, and also the nonionized form iso-C_3H_7OH, whose concentration decreases.

Fig. 1. Dependence of the effective rate constant on sulfuric acid concentration at $C_{\text{sp}} = 0.5$ mol/l.
1—35°, 2—40°, 3—50°, 4—54°, 5—60°.

From the data shown in Fig. 1, the dependence of k_{eff} on temperature was obtained. With an increase in the concentration of H_2SO_4 from 45 to 60%, the effective activation energy E_{eff} at $C_{\text{sp}} = 0.5$ mol/l decreases from 28 to 16 kcal/mol. The change in E_{eff} with acid concentration is a consequence of the fact that k_{eff}, as follows from equation (6), is a complex quantity which, along with the rate constant of the limiting step, includes the ionization constants of iso-C_3H_7OH and TPC and the quantities C_0 and h_0 (^{5,7}). The values of the

Fig. 2

Figure 1: Fig. 2

true rate constant k_0 and the protonation constant of iso-C_3H_7OH, K_{ROH}, can be calculated with the aid of

equation (6). For this purpose it is convenient to use a graphical method. Denoting the factor $K_{\text{ArCOH}}C_\theta/(1+K_{\text{ArCOH}}C_0)=b$, we write equation (6) in the form:

$$\frac{k_{\text{eff}}}{bC_{\text{sp}}}=k_0-K_{\text{ROH}}\frac{k_{\text{eff}}}{bC_{\text{sp}}}. \tag{7}$$

Plotting the dependence of $\frac{k_{\text{eff}}}{bC_{\text{sp}}}$ and $\frac{k_{\text{eff}}}{bC_{\text{sp}}}h_0$, we obtain a straight line cutting off on the ordinate axis a segment equal to k_0. From the slope of the straight line we find the value K_{ROH}. An example of such a dependence for $C_{\text{sp}}=0.1$ mole/liter at 40° is shown in Fig. 2. To construct this dependence we used values of k_{eff} obtained by interpolation of kinetic curves for alcohol concentration $C_{\text{sp}}=0.10$ mole/liter, assuming that such a small concentration does not lead to a decrease in the acidity function H_0 and C_0 (7). The obtained k_0 and K_{ROH} are presented in Table 2.

Fig. 2. Graphical determination of the true rate constant and pK_B^* of isopropyl alcohol at 40° and $C_{\text{sp}}=0.1$ mole/liter

From these data the true activation energy of the reaction under study and the pre-exponential factor were calculated. Fig. 3 shows the graph for calculating the true activation energy. The value found, $E_{\text{true}}=21000\pm500$ cal/mole, in contrast to E_{eff}, is not a function of acid concentration. The pre-exponential factor A in the equation

$$k_0=Ae^{-E_{\text{true}}/RT},$$

equal to $2.81\cdot10^{12}$ liters/mole • sec, practically coincides with the number of binary collisions $Z_0=1.59\cdot10^{12}$, calculated by the formula for the gas phase:

$$Z_0=\frac{N_0}{1000}(r_1+r_2)^2\left[8\pi kT\left(\frac{1}{m_1}+\frac{1}{m_2}\right)\right]^{1/2},$$

where $r_{1\,\text{iso-C}_3\text{H}_7\text{OH}}=3.12$ Å, and r_2—the radius of the arylmethyl cation—is taken as $r_{\text{TPK}}=4.43$ Å (the radii were calculated from average molar volumes).

Fig. 3. Temperature dependence of the true constant of hydride transfer

Fig. 3

Figure 2: Fig. 3

The quantitative agreement obtained between the values A and Z_0 in the case of a reaction between two polyatomic molecules seems to contradict the theory of absolute reaction rates (8). Apparently, however paradoxical this may be, in hydride-transfer reactions (as also in a number of other reactions in solutions (9)), when a linear activated complex is formed, only the reaction centers of the arylmethyl cation and the alcohol should be taken into account,

$$\delta{+}\mathrm{C} \cdots \mathrm{H}^- \cdots \delta{+}\ \mathrm{C}$$

without taking into account either the internal degrees of freedom of the polyatomic molecules or their interaction with the solvent.

From the data of Table 2, the heat and entropy of protonation of isopropyl alcohol were calculated: $\Delta H = 9800 \pm 700$ cal/mole and $\Delta S = +16.8 \pm 0.15$ cal/mole • deg, whence the change in free energy in the reaction

$$\text{iso-C}_3\text{H}_7\text{OH} + \text{H}_3\text{O}^+ \rightleftharpoons \text{iso-C}_3\text{H}_7\text{OH}_2^+ + \text{H}_2\text{O}$$

at 298°K is $\Delta F = 4800$ cal/mole.

It is interesting that the corresponding quantities for methyl alcohol, calculated by us from data (10), are: $\Delta H = 4600$ cal/mole, $S = 12.5$

and $\Delta F = 880$ cal/mole at 298°K. The positive entropy change of the reaction in both cases is close; however, judging by the magnitude of ΔF, methyl alcohol is more basic. The increase in entropy should evidently be attributed to the fact that upon protonation the smaller ion H_3O^+ is converted into the larger ion iso-$\text{C}_3\text{H}_7\text{OH}_2^+$, with a simultaneous decrease in the ordering of the solvent molecules located in the solvation shell of the ion.

Table 2

Temperature dependence of k_0 and K_{ROH}

	35°C	40°C	50°C	54°C	60°C
$k_0 \cdot 10^3$, l/(mole · sec)	4.02	6.25	18.20	29.40	53.90
$K_{\text{ROH}} \cdot 10^3$, l/mole	0.574	0.65	1.008	1.41	1.78
pK_B^*	−3.24	−3.19	−3.00	−2.85	−2.75

[*] $K_B = 1/K_{\mathrm{ROH}}$ –basicity constant of the alcohol,

$$pK_B = -\lg K_B$$

The negative entropy of the reaction in the case of ionization of arylcarbinols may be a consequence of the fact that the arylmethyl cation formed, unlike the alkoxonium ion, has one unoccupied orbital. Therefore it can be solvated not only electrostatically, but also partly through coordination bonding of solvent molecules or anions present in the solution (11). The appearance of the arylmethyl cation leads to still greater ordering of the particles in the solution and thus to a decrease in the entropy of the system.

On the basis of the calculations we obtain

$$k_0 = 2.81 \cdot 10^{12} e^{-21000/RT}, \qquad K_{\mathrm{ROH}} = 4.68 \cdot 10^3 e^{-9800/RT},$$
$$K_{\mathrm{ArCOH}} = 1.05 \cdot 10^{-4} e^{-3280/RT}. \tag{8}$$

Using these quantities, the expression for the effective rate constant can be written in numerical form as

$$k_{\mathrm{eff}} = 2.81 \cdot 10^{12} e^{-21000/RT} \left[\frac{1.05 \cdot 10^{-4} e^{-3280/RT} c_0}{1 + 1.05 \cdot 10^{-4} e^{-3280/RT} c_0} \right] \cdot \left[\frac{1}{1 + 4.68 \cdot 10^3 e^{-9800/RT} h_0} \right]. \tag{9}$$

Expression (9) makes it possible to explain quantitatively the change in E_{eff} with a change in the concentration of sulfuric acid. In the limiting cases, when the acid concentration is small and $K_{\mathrm{ArCOH}} c_0 \ll 1$ and $K_{\mathrm{ROH}} h_0 \ll 1$, the expression for k_{eff} will have the form

$$k_{\mathrm{eff}} = 2.81 \cdot 10^{12} e^{-21000/RT} \cdot 1.05 \cdot 10^{-4} e^{-3280/RT} c_0,$$

i.e. $E_{\mathrm{eff}} = 21000 + 3280 = 24280$ cal/mole; but if the acid concentration is sufficiently large and $K_{\mathrm{ArCOH}} c_0 \gg 1$, $K_{\mathrm{ROH}} h_0 \gg 1$, then the expression for k_{eff} will have the form

$$k_{\mathrm{eff}} = 2.81 \cdot 10^{12} e^{-21000/RT} \cdot 2.13 \cdot 10^{-4} e^{9800/RT} \frac{1}{h_0},$$

i.e. $E_{\mathrm{eff}} = 21000 - 9800 = 11200$ cal/mole.

Institute of Chemical Physics
Academy of Sciences of the USSR

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CITED LITERATURE

1. R. Stewart, Canad. J. Chem., **35**, 766 (1957).

2. P. D. Bartlett, I. D. M. Collum, Am. Chem. Soc., **78**, 1441 (1956).

3. J. Roček, J. Krupička, Collection, **23**, 2068 (1958).

4. J. Krupička, J. Kadlec, Collection, **24**, 1783 (1959).

5. A. I. Gel' bshtein, G. G. Shcheglova, M. I. Temkin, ZhFKh, **1**, 506 (1956).

6. N. C. Deno, J. J. Jaruzelski, A. Schriesheim, J. Am. Chem. Soc., **77**, 3044 (1955).

7. S. G. Entelis, G. V. Epplé, N. M. Chirkov, DAN, **130**, 826 (1960).

8. S. Glasstone, K. Laidler, G. Eyring, *Theory of Absolute Reaction Rates*, IL, 1948.

9. E. A. Moelwin-Hughes, *The Kinetics of Reactions in Solution*, Oxford, 1947, p. 76.

10. H. A. Smith, J. Am. Chem. Soc., **61**, 254 (1939).

11. S. G. Entelis, K. S. Kazanskii, N. M. Chirkov, DAN, **132**, 1152 (1960).

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