

KINETIC SOLVENT EFFECT IN ETARD'S REACTION

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ABSTRACT

The rate of the reaction of chromyl chloride with toluene has been measured in a number of halogenated solvents. The data were correlated with the solubility parameters of the solvents and also with their dielectric constants. The results were taken as evidence against an ionic mechanism for the reaction.

INTRODUCTION

The initial stage of Etard's reaction may involve ionic or molecular attack upon the hydrocarbon by a species containing chromium VI. However, the kinetic study reported previously (1) was unable to discriminate between these two possibilities. In an attempt to subject this point to experimental scrutiny, we have now examined the effect of solvent on the rate of reaction of chromyl chloride with toluene. The influence of solvent on the rate of a chemical reaction has been discussed by Frost and Pearson from two points of view (2, pp. 132, 140). Following Hildebrand (3) they derive a relation between the rate constant and the molar volumes and solubility parameters of the various species (2, p. 132), which can be rearranged:

$$RT \ln (k/k_0) = (V_A \delta_A^2 + V_B \delta_B^2 - V_{\ddagger} \delta_{\ddagger}^2) - 2(V_A \delta_A + V_B \delta_B - V_{\ddagger} \delta_{\ddagger}) \delta_l + (V_A + V_B - V_{\ddagger}) \delta_l^2. \quad [1]$$

Here V represents a molar volume and δ a solubility parameter (related to internal pressure). The subscripts refer to the two reactants (A, B), the activated complex (\ddagger), and the solvent (l), and k_0 and k are the rate constants in a hypothetical ideal solution and in the real solution. For a given reaction at constant temperature, in different solvents having a range of values of the solubility parameter δ_l , by fitting an equation of the form $\log k = a + b\delta_l + c\delta_l^2$ to the data, it should be possible to evaluate V_{\ddagger} from the coefficient of δ_l^2 , and then δ_{\ddagger} from the coefficient of δ_l , if V_A , V_B , δ_A , δ_B are known or can be estimated. With imprecise data it should still be possible, by making an assumption about the volume of activation ($\Delta V_{\ddagger} = V_{\ddagger} - V_A - V_B$), to arrive at an estimate of δ_{\ddagger} , and hence obtain some idea of the molecular character of the activated complex.

The other approach (2, p. 140), following Kirkwood (4), considers all the species A, B, and \ddagger as more or less polar, ignores all but electrostatic forces, and yields

$$RT \ln (k/k_0) = \frac{N(\epsilon-1)}{2\epsilon+1} \left(\frac{\mu_A^2}{r_A^3} + \frac{\mu_B^2}{r_B^3} - \frac{\mu_{\ddagger}^2}{r_{\ddagger}^3} \right). \quad [2]$$

Here k is the rate constant in the real solvent of dielectric constant ϵ , and k_0 is that in a hypothetical solvent of dielectric constant unity, but otherwise identical with the first. N is Avogadro's number, and μ represents the electric dipole moment and r the molecular radius of the species indicated by the subscript. Thus, if estimates can be made of the dipole moments and the radii of the reactant species and of the radius of the activated complex, an estimate of the dipole moment of the complex can be obtained from the slope of a graph of $\log k$ against $(\epsilon-1)/(2\epsilon+1)$.

METHOD AND RESULTS

Kinetic measurements were made on the reaction between chromyl chloride and toluene (Etard's reaction), using the method already described (1), in a number of solvents. The solvents are listed in Table I, together with values of their dielectric constants and

TABLE I
Solvent properties

Solvent	ϵ_{298} *	δ_{298}
1,2-Dichloroethane	10.13	9.8†
1,1,2,2-Tetrachloroethane	7.83	9.8§
Chloroform	4.96	9.3†
1,1,2-Trichloro- <i>f</i> -ethane	2.48†	7.2§
Carbon tetrachloride	2.23	8.6†
Pentachloroethane	3.60	9.4†

*Values from International Critical Tables, unless otherwise indicated.

†Value from "Freon" Technical Bulletin B-2, E.I. du Pont de Nemours and Co. (Inc.), Wilmington 98, Delaware (adjusted to 25° C).

‡Value from ref. 2, p. 436.

§Value estimated by methods from ref. 2, chap. XXIII.

solubility parameters at 25° C. All the solvents were purified by treatment first with concentrated H₂SO₄ and then with water, followed by drying over CaCl₂, and distillation through a short column. The most satisfactory test of purity was found to be the clarity of the CrO₂Cl₂ solutions. Slow reaction of CrO₂Cl₂ with the solvent was observed, and roughly corrected for, in the case of dichloroethane.

Table II contains the results, in the form of second-order rate constants, each being the average of three to six determinations in each solvent at each temperature. Estimates of

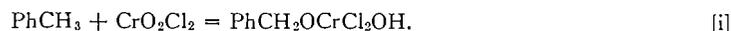
TABLE II
Kinetic data

Solvent	<i>t</i> (°C)	<i>k</i> (liter mole ⁻¹ sec ⁻¹)	<i>E</i> ^a (kcal/mole)	Steric factor
CCl ₄	25.0	1.55 ± 0.04 × 10 ⁻⁴	14.9*	2 × 10 ⁻⁵
C ₂ H ₄ Cl ₂	25.0	7.8 ± 0.6 × 10 ⁻⁴	11.6	1 × 10 ⁻⁶
"	0.4	1.60 ± 0.05 × 10 ⁻⁴		
"	40.0	2.33 ± 0.20 × 10 ⁻³		
CHCl ₃	25.0	2.59 ± 0.14 × 10 ⁻⁴	14.0	1.5 × 10 ⁻⁵
"	35.0	5.84 ± 0.11 × 10 ⁻⁴		
"	1.0	3.28 ± 0.07 × 10 ⁻⁵		
C ₂ H ₂ Cl ₄	27.5	6.28 ± 1.02 × 10 ⁻⁴	13.6	2 × 10 ⁻⁵
"	35.0	1.16 ± 0.11 × 10 ⁻³		
"	1.0	7.4 ± 2.1 × 10 ⁻⁵		
C ₂ Cl ₃ F ₃	1.0	1.83 ± 0.09 × 10 ⁻⁵	14.9	5 × 10 ⁻⁵
"	13.0	5.63 ± 0.08 × 10 ⁻⁵		
"	21.3	1.38 ± 0.25 × 10 ⁻⁴		
C ₂ HCl ₅	0.5	2.5 ± 0.5 × 10 ⁻⁵	14.2	2 × 10 ⁻⁵
"	25.0	2.54 ± 0.15 × 10 ⁻⁴		
"	40.0	7.7 ± 0.7 × 10 ⁻⁴		

*Stairs and Burns (1).

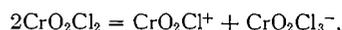
the Arrhenius activation energies and steric factors are also listed. The steric factors appear to be normal (2, p. 94) for a bimolecular reaction between two fairly complex molecules, except for the reaction in 1,2-dichloroethane, which may be anomalously slow, or in error owing to reaction with the solvent. The constants were based on initial rates

only, and are assumed to refer to the first stage of the complex overall reaction, i.e. to the reaction



DISCUSSION

Equation [i] may represent a molecular reaction, going essentially as written, or it may involve attack by a cation derived from CrO_2Cl_2 . In the latter case it is necessary to assume a bimolecular ionization step, e.g.



in order to explain the observed (1) partial order of unity with respect to CrO_2Cl_2 . The activated complex would be cationic, but associated with an anion, and the dipole moment of this ion pair would be large, possibly as large as 10 debyes. If a meaningful solubility parameter could be assigned to such a polar entity, it would be large number. On the other hand, the molecular reaction would be expected to have an activated complex resembling a moderately polar molecule. It should be pointed out that the kinetic ambiguity between ionic and molecular mechanisms demonstrated by Weil and Morris (5) in the urea reaction does not apply here, owing to the distinctly different character of the activated complex postulated for the two mechanisms.

Figure 1(a) shows the results of plotting the logarithms of the observed rate constants versus the solubility parameters (δ_i) of the various solvents, all at 25° C. The data did not

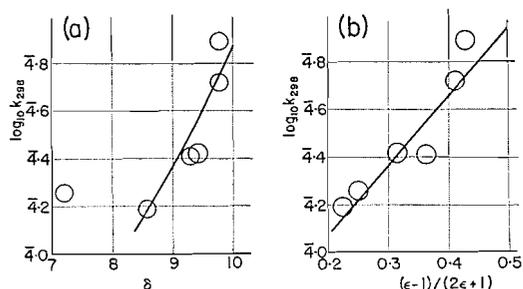


FIG. 1. Rate constants at 25° C in various solvents (as common logarithms) plotted (a) against the solubility parameters of the solvents, δ_i , and (b) against the function $(\epsilon-1)/(2\epsilon+1)$ of the dielectric constant.

appear to fit equation [1] well enough to justify calculation of the volume of activation, so the curve in the figure was drawn with an assumed value of $\Delta V_{\ddagger} = -10$ ml/mole. The point for the solvent $\text{CF}_2\text{ClCFCl}_2$ is the only one seriously off the curve.

The positive slope means that the activated complex has a higher solubility parameter than the reactants. Using molar volumes and solubility parameters of 107 ml and 8.9 for toluene (3, p. 437) and 81.0 ml and 10.4 for CrO_2Cl_2 (estimated by methods of ref. 3, chap. XXIII), the value of δ_{\ddagger} estimated from the slope is 11.5 ± 0.5 , which represents only a moderate increase in intermolecular forces, and presumably in polarity.

In Fig. 1(b) the logarithms of the observed rate constants are plotted against $(\epsilon-1)/(2\epsilon+1)$ at 25° C. The positive slope of the line means that the activated complex is more polar than the reactants. Using radii estimated from the molar volumes used above, and the dipole moments 0.47 for CrO_2Cl_2 (6) and 0.4 (7) for toluene, one may calculate from the slope, using equation [2], $\mu_{\ddagger} = 2.0$. This value is typical of moderately polar molecules.

Analysis of the data by the two methods has shown that, in this case at least, the data are more compatible with the electrostatic than with the solubility parameter theories. However, within their limitations both approaches lead to the same conclusion, namely that the activated complex in Etard's reaction is somewhat more polar than the starting materials, but probably not polar enough to be described as ionic, even though in these relatively non-polar media an ionic activated complex would probably exist as an associated ion pair.

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