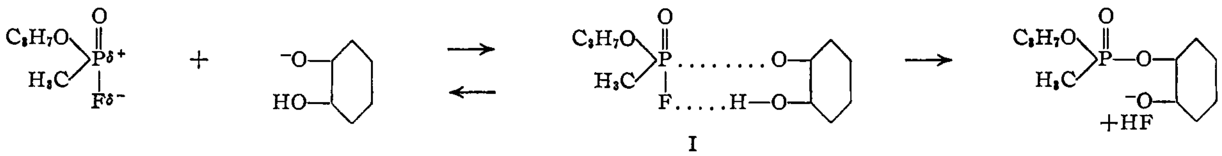
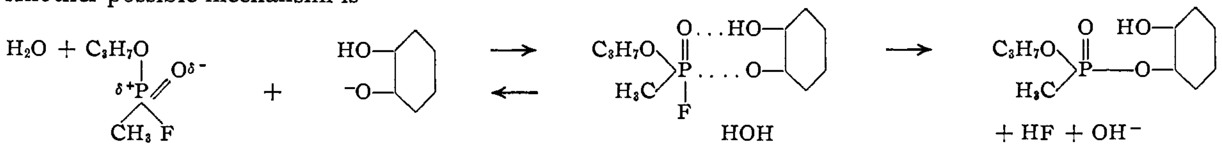


I

Another possible mechansim is



trations of the complexes (such as I) formed for two catechols of very different basicities may be close to one another due to the differences in the concentrations of the monocatecholate ions. This is the reason that all shown k_2' values are of the same order of magnitude. This can be shown more clearly from the experimentally derived relationship between the rate constants and the basicity of the catecholate ion. Since $k_2 = 2.57 \times 10^{-6} K_B^{0.89}$ and $k_2 = k_2'(K_B[H^+] + 1)$

$$k_2' = 2.57 \times 10^{-6} K_B^{0.89}/(K_B[H^+] + 1)$$

Thus considering the reactivities of two catechols at pH 6, one having a basic dissociation constant of 10^7, the other 10^{10}, it is clear that the k_2' values will vary only by 3 to 4 times. By differentiating k_2' with respect to K_B, it can further be shown that, at a given pH, the maximum attainable value of k_2' will be reached at $K_B = 8.1/[H^+]$. Thus, the answer to the question as to which of the nuclearly substituted catechols will have the maximum reactivity with Sarin depends on the pH at which such reactivity is desired.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Molecular Compounds. VI. A Reinvestigation of the Picryl Chloride–Hexamethylbenzene Complex; The Effect of Triethylamine on the Equilibrium Constant for Complex Formation

BY SIDNEY D. ROSS, MORTIMER M. LABES AND MEYER SCHWARZ

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The picryl chloride–hexamethylbenzene complex has been studied in chloroform containing 0.75% ethanol and 93% chloroform–7% ethanol. It is shown that the differences in the equilibrium constants as determined by the spectroscopic method and as measured by the reaction rate method may be attributable to solvation and stabilization of the complex by triethylamine.

In a previous investigation in this Laboratory,[1] the equilibrium constant for complex formation in chloroform between picryl chloride and hexamethylbenzene was determined by a spectroscopic method and a method based on determinations of reaction rates. The latter method gave a value for the equilibrium constant which was more than ten times larger than the spectroscopic value of 0.073 ± 0.009 l. mole^{-1}. The spectroscopic value was taken as a measure of the complexing due to formation of a charge–transfer intermolecular bond, and the larger value, obtained from the reaction rate measurements, was rationalized, by postulating additional interactions capable of affecting the rate of the reaction between picryl chloride and triethylamine.

The reinvestigation of this system was motivated by three major considerations. All of our previous measurements were made in pure chloroform. In the absence of a stabilizer, usually ethanol, chloroform is subject to air oxidation and resultant contamination by traces of phosgene. It seemed, therefore, pertinent to demonstrate that the previously reported results were not due to solvent instability. More important, Profs. E. Grunwald and J. E. Leffler pointed out to us that for the case of multiple equilibria with only one complex being colored, the spectroscopic method should result in an over-all equilibrium constant which sums all of the complexes.[2] Finally, our study of solvent effects on molecular complexing[3] suggested to us the possibility that the discrepancy between the spectroscopic equilibrium constant and the one derived from the rate studies might be due to solvation and stabilization of the picryl chloride–

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[1] S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, THIS JOURNAL, 76, 69 (1954).

[2] Private communication from Profs. E. Grunwald and J. E. Leffler of the Florida State University. For the case of A and B in equilibrium with a series of complexes, AB, with only one of these complexes being colored

$$[A] = [A_0] - \Sigma_i[AB_i]$$
$$[B] = [B_0] - \Sigma_i[AB_i]$$
$$[AB]\text{colored} = f\Sigma_i[AB_i] = \frac{d}{\epsilon_{AB}}$$

where f is the fraction of the total complexes that is colored.

$$d = f\epsilon_{AB}\Sigma_i[AB_i] = \epsilon_{\text{apparent}}\ \Sigma_i[AB_i]$$

and the equilibrium constant actually determined is given by

$$K = \Sigma_i[AB_i]/[A][B]$$

[3] S. D. Ross and M. M. Labes, THIS JOURNAL, 77, 4916 (1955).

hexamethylbenzene complex by triethylamine. It is to be remembered that triethylamine is always present in appreciable concentration in the rate experiments and always absent in the spectroscopic experiments.

Experimental

The experimental methods have been fully described.[1] Measurements were made in chloroform stabilized with 0.75% ethanol, a C.P. reagent with the ethanol added by the manufacturer, and in 93% chloroform–7% ethanol, an azeotrope prepared by distillation and boiling at 59.35°.[4] The picryl chloride, triethylamine and hexamethylbenzene were purified as before[1] and had the previously reported physical constants. 1,3,5-Trinitrobenzene, Eastman Kodak Co. White Label, was crystallized from chloroform as almost colorless needles, m.p. 121°.

Results

The equilibrium constants for formation of the picryl chloride–hexamethylbenzene complex in chloroform containing 0.75% ethanol and in 93% chloroform–7% ethanol at 24.8 ± 0.1° have been determined by the spectroscopic method. The values obtained were 0.10 ± 0.01 l. mole^{-1} in the former solvent and 0.16 ± 0.02 l. mole^{-1} in the azeotrope. These values are to be compared with the value of 0.073 ± 0.009 l. mole^{-1}, obtained in pure chloroform at 23.8 ± 0.1°.[1]

Table I presents the rates of the picryl chloride–triethylamine reaction in the absence and presence of hexamethylbenzene in the two solvents at 24.8 ± 0.1°. In calculating the equilibrium constants in 93% chloroform–7% ethanol, we used a value of 0.0660 l. mole^{-1} hr.$^{-1}$ for the rate constant in the absence of hexamethylbenzene. This is the average of the two determinations at an initial amine concentration of 0.36 *M*. In this solvent, the equilibrium constant, as determined by the reaction rate method, is, therefore, more than five times as large as the value obtained by the spectroscopic method.

TABLE I

RATES OF THE PICRYL CHLORIDE–TRIETHYLAMINE REACTION IN THE PRESENCE AND ABSENCE OF HEXAMETHYLBENZENE AT 24.8 ± 0.1° AND CALCULATED EQUILIBRIUM CONSTANTS FOR FORMATION OF THE PICRYL CHLORIDE–HEXAMETHYLBENZENE COMPLEX

Picryl chloride, mole l.$^{-1}$	Triethylamine, mole l.$^{-1}$	Hexamethylbenzene, mole l.$^{-1}$	*k*, l. mole^{-1} hr.$^{-1}$	*K*, l. mole^{-1}
In 93% chloroform–7% ethanol				
0.04943	0.3569	0	0.651	
.04833	.3573	0	.669	
.05080	.2850	0	.638	
.04931	.2136	0	.643	
.04586	.1428	0	.608	
.05258	.1422	0	.604	
.05011	.07194	0	.590	
.04796	.3568	1.00	.363	0.84
.04615	.3545	0.750	.401	.88
.04590	.3562	.500	.469	.84
.03999	.3573	.250	.550	.82
In chloroform containing 0.75% ethanol				
0.05004	0.1423	0	0.299	
.05052	.07172	0	.297	
.04889	.3556	0	.290	
.05092	.07120	1.00	.195	0.52
.05087	.1426	1.00	.180	.65
.05007	.1419	1.00	.176	.73
.04835	.2837	1.00	.171	.74
.04994	.2126	1.00	.179	.66
.05165	.3566	1.00	.152	.96
.05119	.3564	1.00	.155	.93

The data in chloroform containing 0.75% ethanol are of particular interest because they demonstrate the effects of varying amine concentrations. In the absence of hexamethylbenzene a fivefold variation in the amine concentration changes the rate constant by only 3%. In the presence of 1.00 *M* hexamethylbenzene, the same change in the amine concentration causes a change of almost 20% in the rate constant and an even larger change in the calculated equilibrium constant.

Table II presents the data resulting from our study of the effect of triethylamine on the equilibrium constant for formation of the 1,3,5-trinitrobenzene–hexamethylbenzene complex in chloroform containing 0.75% ethanol at 24.8 ± 0.1°.

TABLE II

THE EFFECT OF TRIETHYLAMINE ON THE EQUILIBRIUM CONSTANT FOR FORMATION OF THE 1,3,5-TRINITROBENZENE–HEXAMETHYLBENZENE COMPLEX IN CHLOROFORM CONTAINING 0.75% ETHANOL AT 24.8 ± 0.1°

Triethylamine, mole l^{-1}	Wave length, mμ	ϵ	*K*, l. mole^{-1}
0	450	1576	0.53
	460	1249	.46
	470	693	.58
	480	476	.50
0.0474	440	1947	.57
	450	1483	.58
	460	1017	.60
.109	400	3422	.58
	410	3261	.57
	420	2985	.55
.200	400	3472	.57
	410	3158	.59
	420	2796	.59
.297	400	3138	.65
	410	2849	.67
	420	2428	.70
.498	390	3039	.71
	400	3018	.70

Discussion

In both solvents, the equilibrium constants calculated from the rate studies (Table I) are at least five times as large as the equilibrium constants determined from the spectroscopic measurements. The previously reported results in pure chloroform[1] are, therefore, not in any way attributable to the instability of pure chloroform. It is the purpose of this paper to advance and explore the hypothesis that the high values obtained for the equilibrium constants for formation of the picryl chloride–hexamethylbenzene complex from the rate measurements are the result of solvation and stabilization of the complex by triethylamine.

This hypothesis was tested by investigating the

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(4) "Azeotropic Data," American Chemical Society, Washington, D. C., 1952, p. 21.

dependency of the calculated equilibrium constants on the initial amine concentrations used in the rate measurements of the picryl chloride–triethyl amine reaction in chloroform containing 0.75% ethanol (Table I). In this solvent, in the absence of hexamethylbenzene, the amine concentration could be varied fivefold, and the rate constant changed by only 3%. However, for the same range of amine concentrations in the presence of 1.00 M hexamethylbenzene, the average value for the rate constant is 0.173 l. mole^{-1} hr.$^{-1}$, and the maximum deviation from this average value is more than 13%. The effect is magnified still further in the equilibrium constant. The average value is 0.74 l. mole^{-1}, and the maximum deviation from this average is almost 30%.

The effect due to triethylamine is thus definite and operates in the right direction, for the equilibrium constants increase with increasing initial amine concentration. The remaining question is whether or not this effect can account quantitatively for the total discrepancy between the spectroscopic equilibrium constants and the constants obtained from the rate studies. If the equilibrium constants depended on some function of the amine concentration such that all the data could be fitted smoothly and the extrapolated value at zero amine concentration corresponded to the value obtained from the spectroscopic measurements, this would represent a positive answer to the question which we have raised.

To determine the best possible linear fit we plotted log K *vs.* log (amine) and calculated the slope of the best straight line through the points by the method of least squares. The value obtained for the slope was 0.397. A plot of K *vs.* (amine)$^{0.397}$ is linear, and for this function of the amine concentration, the equilibrium constant at zero amine concentration is within 2% of the spectroscopically determined value. The maximum deviation from the least squares line is 13%, and the average deviation is less than 6%. This is as good a fit as can be expected, particularly when it is remembered that the uncertainties in the equilibrium constants determined by this method are large.

However, because the uncertainties in equilibrium constants calculated from rate measurements are large and because we can offer no facile rationalization for this particular dependency on the amine concentration, we have investigated the effect of triethylamine on the equilibrium constant for formation of the 1,3,5-trinitrobenzene–hexamethylbenzene complex (Table II). This complex was chosen because of its structural similarity to the picryl chloride–hexamethylbenzene complex and because, in this case, we could measure the equilibrium constants by the more direct spectroscopic method.

The results (Table II) show some scattering, but there is a definite increase in the equilibrium constant with increasing amine concentration: from 0.52 l. mole^{-1} in the absence of amine to 0.71 l. mole^{-1} with 0.498 M triethylamine present. The average of all the determinations at all the amine concentrations is 0.59 l. mole^{-1}, and the maximum deviation from this average value is almost 20%. Since in any set of measurements at a single amine concentration, the maximum deviation from the average value was never as high as 10%, the effect due to triethylamine is not attributable to experimental error.

These data can be fitted well, within experimental error, by plotting K *vs.* (amine), (amine)$^{1/2}$ or (amine)$^{1/3}$. Almost equivalent linear fits are obtained in all three cases, and a plot of K *vs.* (amine) is representative. For such a plot, the maximum deviation of any point from the least squares line through all the experimental points is 6.0%, and the average for all the deviations is 3.6%.

Although those results demonstrate the effect of amine, the measurements are not sufficiently precise to define a specific dependency on the triethylamine concentration. Perhaps it is, after all, unrealistic to demand a unique, linear dependency on the amine concentration. Solvation is a complicated and not fully understood process. It is sufficient for our purpose to demonstrate that it is consistent with the experimental data to attribute the large discrepancy between the equilibrium constant for formation of the picryl chloride–hexamethylbenzene complex as determined by the spectroscopic method and from rate studies to solvation and stabilization of the complex by triethylamine.

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