Reaction of Picryl Chloride with Sodium Ethoxide: Formation of a C 3 σ -Complex

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Abstract

Kinetic and spectroscopic evidence is presented for the formation of a C3 σ -complex from picryl chloride and sodium ethoxide in ethanol. Molar extinction coefficients of the complex were determined by the Benesi-Hildebrand method. Thermodynamic parameters were evaluated.

Introduction

The formation of the Meisenheimer complex (1) from 2,4,6-trinitroanisole (tna) and methoxide ion was first found by Servis¹ from n.m.r. studies in dimethyl sulphoxide (Me₂SO) to be preceded by a much faster formation of an isomeric C3 complex (2).



Since then many other C3 complexes have been reported.²⁻⁶ It is generally observed that the C3 complex is thermodynamically less stable than its C1 isomer. The stability of the C3 complex, however, is found to be higher in dipolar aprotic than in protic media. Hence most of the C3 complexes have been observed in Me₂SO or Me₂SO solvent-mix. Because of the less stable nature of the C3 complex, kinetic data are meagre. Only recently was Bernasconi⁷ able to obtain full kinetic data for the formation of (2) in a protic solvent, i.e. methanol, with a combined stopped-flow temperature-jump technique. More recently in a study of nucleophilic substitution of picryl chloride (3) by methoxide ion in methanol, a C3 complex (4; R = Me) was also observed. However, some difficulties were experienced from obtaining

- ³ Fendler, E. J., Griffin, G. E., and Fendler, J. H., Tetrahedron Lett., 1968, 5631.
- ⁴ Fendler, E. J., Fendler, J. H., Griffin, G. E., and Larsen, W. J., J. Org. Chem., 1970, 35, 287.
- ⁵ Terrier, F., and Millot, F., C. R. Acad. Sci., Ser. C, 1969, 268, 808.
- ⁶ Millot, F., and Terrier, F., Bull. Soc. Chim. Fr., 1969, 2694.
- ⁷ Bernasconi, C. F., J. Amer. Chem. Soc., 1971, 93, 6975.

¹ Servis, K. L., J. Amer. Chem. Soc., 1967, 87, 5495.

² Fendler, J. H., Fendler, E. J., and Griffin, G. E., J. Org. Chem., 1969, 34, 689.

accurate kinetic data from stopped-flow experiments, due to the low stability and high reverse rate constant of (4; R = Me).⁸



The objectives of this research were twofold—to gain more evidence that a C3 complex is formed from (3) and alkoxide ion before replacement of the chlorine atom occurs and to obtain more accurate kinetic and thermodynamic parameters of a C3 picryl chloride complex. By analogy to the interactions of 1,3,5-trinitrobenzene (tnb) with alkoxide ions in their respective alcohols,⁹ a higher stability and lower reverse rate constant for (4; R = Et) in ethanol are expected. These are now confirmed.

Experimental

Reagents

Eastman picryl chloride was purified as described previously.⁸ Absolute ethanol from James Burrough Ltd was dried over 1/8-in. molecular sieve pellets, type 4A from Union Carbide, and distilled. The middle portion of the distillate was collected.

Stock solutions of sodium ethoxide were prepared as usual and standardized with HCl to the phenolphthalein end-point. Solutions of lower concentrations were prepared by dilution.

Equilibrium and Kinetic Studies

A Durrum-Gibson D-110 stopped-flow spectrophotometer connected with a Tektronix R5103N oscilloscope was used for both kinetic and equilibrium studies. The cuvette of the spectrophotometer has an optical path length of 2 cm. The optical density obtained from the stopped-flow spectrophotometer was checked and found to agree with the value obtained on a Beckman DB-G spectrophotometer.

In all runs, the concentrations of (3) were kept constant $(2 \cdot 17 \times 10^{-5} \text{M})$ and the base concentrations were about 100 times in excess. The reactions thus followed a simple pseudo-first-order rate law. Whenever new solutions were introduced into the drive syringes, they were allowed to stand for 20 min in order to reach thermal equilibrium with the bath. The temperatures of the bath were controlled to an accuracy of 0.1° C.

For the equilibrium studies the optical densities at 'infinite time' (D_{∞}) were recorded. The molar extinction coefficient (ε) and the equilibrium constant (K) were evaluated from the Benesi-Hildebrand (B-H) equation.¹⁶

Results and Discussion

When sodium ethoxide is added to a solution of (3) in ethanol, the red colour developed is preceded by another very fast colour formation which can only be monitored on an oscilloscope connected to a stopped-flow spectrophotometer. The final red species is believed to be the 1,1-diethoxy-2,4,6-trinitrohexadienate anion (5) by



⁸ Gan, L. H., and Norris, A. R., *Can. J. Chem.*, 1974, **52**, 18. ⁹ Gan, L. H., and Norris, A. R., *Can. J. Chem.*, 1971, **49**, 2490.

¹⁰ Benesi, H., and Hildebrand, J., J. Amer. Chem. Soc., 1949, 71, 2703.

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analogy to the interaction of (3) with methoxide ion.⁸ The fast colour formation is identified to be due to (4; R = Et). A simultaneous slower attack of ethoxide ion at C1 would lead to the release of chloride ion, giving 2,4,6-trinitrophenetole as a product. With excess ethoxide ion, further attack of the base would give the thermodynamically more stable (5) as the final coloured species.

The kinetic and equilibrium data for reaction (1)

$$(3) + \text{EtO}^{-\frac{k_1}{k_{-1}}}(4; \ \mathbf{R} = \text{Et}) \tag{1}$$

can be conveniently determined with a stopped-flow spectrophotometer. The rate of formation of (4; R = Et) is very fast and equilibrium is established before the attack of the base at C1 occurs. The visible spectrum of (4; R = Et) was obtained by measuring the optical densities at equilibrium (D_{∞}) at different wavelengths. The equilibrium constant (K) and the molar extinction coefficient (ε) of (4; R = Et) at



Fig. 1. The B-H plot of $[(3)]_0/D_\infty$ against $[NaOEt]^{-1}$ at various temperatures.

Table	1.	Eq	uilil	oriur	n i	con	stan	its	and	mo	lar	extin	iction
coe	effici	ents	of	(4;	R		Et)	de	termi	ned	at	480 n	m
Error	lim	ite	0 * 0	hae	ьđ	01	+h					hatad	with

Error limits are based on the errors associated with the least squares slopes and intercepts of the B-H plots

Temp. (°C)	$10^{-4}\varepsilon$ (l. mol ⁻¹ cm ⁻¹)	K (l. mol ⁻¹)
12.2	$2 \cdot 15 \pm 0 \cdot 04$	347 ± 12
18.2	$2 \cdot 22 \pm 0 \cdot 05$	380 ± 22
30.0	$2 \cdot 08 \pm 0 \cdot 05$	440 ± 28

480 nm were evaluated by the B-H method. Plots of $[(3)]_0/D_{\infty}$ against $1/[\text{EtO}^-]$ are linear at all temperatures (Fig. 1), indicating that the complex is formed with 1:1 stoichiometry. All three plots have roughly the same intercept which is equal to $1/\epsilon l$, where l (2 cm) is the optical path length. The slope is equal to $1/\kappa\epsilon l$. The ratio of intercept to slope yields K. Results thus obtained are presented in Table 1.

The visible spectra of (4; R = Et) and also of the tnb-ethoxide complex in ethanol are shown in Fig. 2. The ε values of (4; R = Et) at the long wavelength absorption maximum are significantly higher than those of the tnb-ethoxide

complex,^{10*} whereas those at the shorter wavelength are roughly the same for both complexes. The spectrum is typical of a C3 picryl chloride complex. In the present system where $K \approx 300 \, \text{l. mol}^{-1}$ for reaction (1) at the temperatures studied, ε values obtained by the B-H method should be of reasonable accuracy since a saturation fraction, i.e. a ratio of the concentration of the complex to the initial concentration of the dilute component of 0.2-0.8, is attained.¹¹



Fig. 2. Visible spectra of σ -complexes in ethanol at 25°C. A, (4; R = Et); B, tnb-ethoxide complex. Fig. 3. Plots of k_{obs} as a function of sodium ethoxide concentration at various temperatures.

Table	2.	Rate	constants	for	the	formation	and	decomposition	of
				(4;	R	$= \mathbf{E}\mathbf{t}$)			

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Temp. (°C)	k_1 (l. mol ⁻¹ s ⁻¹)	k_{-1} (s ⁻¹)	k_1/k_{-1} (l. mol ⁻¹)
12.2	2750 ± 78	10.0 ± 0.3	276 ± 16
18.2	3950 ± 81	$13 \cdot 9 \pm 0 \cdot 3$	284 ± 12
$25 \cdot 0$	5770 ± 277	19.7 ± 0.9	293 ± 28
30.0	7900 ± 182	$26 \cdot 5 \pm 0 \cdot 6$	298 ± 14

Error limits for k_1 and k_{-1} are based on the errors associated with the least-squares slopes and intercepts of plots of k_{obs} against [NaOEt]

All the kinetic runs were carried out with base concentrations in excess. The pseudo-first-order rate constant k_{obs} where

$$k_{\rm obs} = k_1 [{\rm EtO}^-] + k_{-1}$$

was obtained from the slope of a plot of $\ln(D_{\infty} - D_t)$ against time. No attempt was made to control the ionic strength of the solution. Plots of k_{obs} against ethoxide concentration are all linear (Fig. 3), indicating little variation in activity of the ethoxide ion at the concentration range studied. Ion pairing is also not a

^{*} Reinvestigation has shown that the tnb-ethoxide complex has e_{max} of 1.48×10^4 and 1.73×10^4 l. mol⁻¹ cm⁻¹ at 427 and 497 nm. These values are consistent with other tnb-alkoxide complexes.

¹¹ Deranleau, D. A., J. Amer. Chem. Soc., 1969, 71, 2703.

problem.⁹ Values of k_1 and k_{-1} were obtained from slopes and intercepts of plots of k_{obs} against [EtO⁻] by a linear regression method. Results are presented in Table 2.

The ratios of k_1/k_{-1} , theoretically equal to K, are found to be consistently lower than those obtained by the B-H method. Such discrepancies between the K values obtained from the kinetic and equilibrium studies have also been noted in other systems.^{9,12} However, both methods give higher K values at higher temperatures, agreeing qualitatively that reaction (1) is endothermic.

The thermodynamic parameters obtained from plots of the logarithm of the rate constants against 1/T are

ΔH_1	=	40	±2	kJ mol ⁻¹	ΔS_1	=	$-38\cdot5\pm$	8·4 J	K-1	mol^{-1}
ΔH_{-1}	=	37	±2	kJ mol ⁻¹	ΔS_{-1}	=	$-98\cdot5\pm$	8·4 J	K-1	mol^{-1}
ΔH°	=	3.3	± 4.2	kJ mol ⁻¹	ΔS°	=	57 · 3 ± 3	16·7 J	K-1	mol ⁻¹

Con- stant	(4; $R = Et$) in ethanol	tnb–OEt ^A in ethanol	(4; $R = Me)^B$ in methanol	tnb-OMe ^A in methanol
k_1 (l. mol ⁻¹ s ⁻¹)	5770	49500	912	7700
k_{-1} (s ⁻¹)	19.7	15.4	303	357
k_1/k_{-1} (l. mol ⁻¹)	293	3100	3.01	21.6
K (l. mol ⁻¹)	410	2020	2.58	16.6
^A Ref. 12. ^B R	lef. 9.			

Table 3. Rate and equilibrium constants of some σ -complexes at 25°C

While from the absorption spectrum there is little doubt that the coloured species observed in this study is (4; R = Et), the same conclusion could also be drawn from a comparison of the kinetic and equilibrium data of (4; R = Me and Et) with those of the corresponding tnb-alkoxide complexes (Table 3). The ratios of the rate and equilibrium constants of (4; R = Et) to the tnb-ethoxide complex are identical, within the experimental errors, to the ratios of those of (4; R = Me) to the tnb-methoxide complex. This suggests that the same species are formed from (3) with both alkoxide anions. Furthermore, the almost identical decomposition rate constants of (4; R = Me and Et) and the corresponding tnb-alkoxide complexes are good evidence that the alkoxide ion is bonded to the unsubstituted ring carbon.

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¹² Bernasconi, C. F., J. Amer. Chem. Soc., 1970, 92, 4682.