Charge-transfer Complexes in Organic Chemistry. Part VII.† Influence of Charge-transfer Complexes on the Quaternisation of Triethylamine by Tetrachlorophthalic Anhydride ‡

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The kinetic effect of extra donor molecules on the reaction of tetrachlorophthalic anhydride with triethylamine was examined in different solvents. The inhibition, observed in every case, may arise from association effects and from factors modifying the rate constant. The reactivity of the complex of donors with tetrachlorophthalic anhydride is briefly discussed.

We have studied[1,2] the quaternisation of triethylamine by tetrachlorophthalic anhydride in various aprotic media. The n–π type charge-transfer complex formed between the amine and the anhydride seems to be a real intermediate on the reaction path. Considering that a certain number of reactions seem also to proceed

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through a charge-transfer complex intermediate[3-15] (for reviews see refs. 16 and 17) we further generalised the idea. We postulated that in any reaction a charge-transfer complex is formed between the reagents before they reach the transition state. This complex can be either a 'true'[2] charge-transfer complex or any kind of molecular association. We now examine the possibility of influencing this reaction by the presence of extra complexing agents.[15,18-20]

The observed acceleration or inhibition may have various causes (*e.g.*, electronic, steric, or solvent effects). This catalytic role is more subtle than that of ordinary catalysts, and it may be important especially in biological chemistry.

RESULTS AND DISCUSSION

Apparent first-order rate constants (k'_0) were determined for the reaction of tetrachlorophthalic anhydride with triethylamine at fixed amine concentration. The concentration of the added complexing agents (π-donors) such as acenaphthene, phenanthrene, 2-methoxynaphthalene, 1-methylnaphthalene, and durene was systematically varied and a new apparent first-order rate constant was determined (k_{obs}). The solvent effect was also examined in various aprotic media (tetrahydrofuran, benzene, ethyl acetate, 1,2-dichloroethane, and n-butyl chloride). The equilibrium constants extracted from kinetic data (K_{kin}) were controlled by independent spectroscopic measurements (K_{sp}), a simple kinetic run is given in Table 1.

TABLE 1

Kinetics of reaction of tetrachlorophthalic anhydride (3×10^{-4}M) with triethylamine ($8{\cdot}45 \times 10^{-3}$M) in n-butyl chloride at 20 °C; $\bar{\nu} = 29{\cdot}75$ kK, the absorption band of the anhydride

10[Acenaphthene]/M	0	0·75	1·00	1·5	2·19	3·00
$10k_{obs}$/min^{-1}	1·09	0·82	0·69	0·59	0·43	0·35

The values of the rate constants decrease regularly with increasing donor concentration. The results obtained for all the donors studied in different solvents are in Table 2. In all cases the donor molecules inhibit the reaction. This seems to be a general observation for carbonyl group reactions[17] (but see ref. 18). The inhibitory effect may come from the association of tetrachlorophthalic anhydride with the π-donors or may be accompanied by the modification of the rate constant.

In the first case the complex of tetrachlorophthalic anhydride with a donor does not react, *i.e.*, its pseudo-first-order rate constant k'_c is zero (no reaction) or approximately zero (total inhibition). Equation (1) holds in this case.

$$k'_0/k_{obs} = 1 + K_{kin}[\text{Donor}] \qquad (1)$$

If the complex does react simultaneously (pseudo-first-order rate constant k'_c) this expression becomes (2).

$$\frac{k'_0}{k_{obs}} = \frac{1 + K_{kin}[\text{Donor}]}{1 + \dfrac{k'_c}{k'_0} K_{kin}[\text{Donor}]} \qquad (2)$$

If $(k'_c/k'_0)k_{kin}[\text{Donor}] \ll 1$ the two schemes cannot be distinguished. In favourable cases if the plot of log (k'_0/k_{obs}) against [Donor] is a curve the linear form of equation (2) $\{(k'_0 - k_{obs})^{-1}$ against $[\text{Donor}]^{-1}\}$ may well give a straight line and thus a convenient proof for the reactivity of the complex. For further details and a numerical calculation see refs. 17 and 21. In the quaternation of triethylamine by tetrachlorophthalic anhydride an n-π charge-transfer complex, formed between the two reagents (equilibrium constant K_n), is present on the reaction path.[1,2] This fact complicated the kinetic scheme and the above formulae are valid only in certain conditions (*e.g.*, $K_n[\text{Et}_3\text{N}] \ll 1$).

In all cases studied both equations gave a straight line and therefore it was not possible to decide whether the complex reacted or not. If it is assumed that the complex does react, k'_c could be estimated from the intercept $(k'_0 - k'_c)$ at $[\text{Donor}]^{-1} = 0$ of a plot of $(k'_0 - k_{obs})^{-1}$ against $[\text{Donor}]^{-1}$ (see Table 2). It turned out that $k'_0 - k'_c \approx k'_0$ showing that the value of k'_c is within the experimental error (*ca.* 3%). We conclude that if the complex does react its reactivity is at least 30 times lower than that of free tetrachlorophthalic anhydride. When pure donor 1-methylnaphthalene was used as solvent, the rate constant at the same amine concentration ($2{\cdot}8 \times 10^{-3}$M) was $k'_c = 0{\cdot}75 \times 10^{-3}$ min^{-1}.

The spectroscopically determined equilibrium constants K_{sp} are in reasonable agreement with K_{kin} as shown in Table 2. Similar results are obtained from zero time absorbancy values (K'_{sp}).

Durene has no effect on the reaction rate when the

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experiment is carried out in tetrahydrofuran, possibly owing to the equality $k'_0 \approx k'_c$ or the smallness of K_{kin} or both. On the other hand, in ethyl acetate, durene has a sizeable effect on the rate constant.

The inhibitory effect observed cannot be attributed unequivocally to the reduced reactivity of a reacting complex. Nevertheless if the complex of tetrachlorophthalic anhydride with a donor reacts, steric effects may contribute up to 50% to the overall rate decrease. This is because one side of the flat anhydride molecule is shielded by the donor.[17] Any further decrease must be attributed to other factors (electronic effect, solvation, *etc.*). Surprisingly the polarisability of the donor molecules seems to decrease the reaction rate.[22]

EXPERIMENTAL

Kinetic Measurements.—The disappearance with time of the absorption band of tetrachlorophthalic anhydride (ν̄ 29·5 kK) or its complex (ν̄ 24·5 kK) was followed spectrophotometrically with a Unicam SP 800 apparatus. The temperature was controlled within ±0·1 °C.

Determination of K_{sp}.—K_{sp} values were obtained from absorbancy values by use of the Benesi–Hildebrand equation.[15,23]

Materials.—Tetrachlorophthalic anhydride, triethylamine, and all solvents were purified as described previously.[2] Standard methods of purification were used for the donor molecules.

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TABLE 2

Complexation effect on the reaction of tetrachlorophthalic anhydride with triethylamine at 20 °C

Solvent	Donor	$10^2[Et_3N]$/M	K_{kin} / l mol^{-1}	K_{sp} / l mol^{-1}	$10^3k'_0$ / min^{-1}	$10^3k'_c$ / min^{-1}	10^3k_{obs} † / min^{-1}
Tetrahydrofuran	Acenaphthene	5·375	0·80	0·70	33·6	$\leqslant 1$	25·1
Tetrahydrofuran	Durene	5·375		0·30	33·6	No effect	
Benzene	Acenaphthene	7·0	0·85	1·40	101	$\leqslant 3$	72·0
Ethyl acetate	Acenaphthene	2·8	1·90	1·60	42·5	$\leqslant 1$	23·4
Ethyl acetate	Durene	2·8	1·10	0·90	42·5	16	33·1
1,2-Dichloroethane	Acenaphthene	0·35	0·8	2·0	77	$\leqslant 3$	57·5
1,2-Dichloroethane	Phenanthrene	1·075	1·90	3·20 2·2 *	208	$\leqslant 6$	114·3
1,2-Dichloroethane	2-Methoxynaphthalene	1·075	2·10	1·50 1·35 *	200	$\leqslant 6$	102·0
n-Butyl chloride	Acenaphthene	0·845	5·3	2·90	109	$\leqslant 3$	26·8
n-Butyl chloride	1-Methylnaphthalene	0·28	4·0		36	$\leqslant 1$	12·7

* Values for K'_{sp}. † Donor concentration 0·45M.

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