Charge-transfer Complexes in Organic Chemistry. Part XIII.† Effects of Charge-transfer Complexes on the Reaction of 3,5-Dinitrophthalic Anhydride with Pyridine

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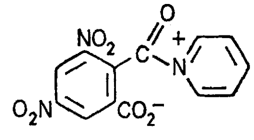
The rate of the reaction of 3,5-dinitrophthalic anhydride with pyridine in organic aprotic media is decreased by the aromatic electron donor, acenaphthene. Kinetic evidence is presented for the reactivity of the charge-transfer complex formed between the donor and the anhydride.

We have previously reported the reaction of tetrachlorophthalic anhydride (TCPA) with tertiary amines.[1] A charge-transfer (CT) complex was detected between TCPA and the amines, and a study of solvent effects suggested that the CT complexes might be intermediates on the reaction path. A general scheme was proposed for nucleophilic reactions of the carbonyl group.

We now report the quaternization of pyridine with 3,5-dinitrophthalic anhydride (3,5-NPA) and the effect of an external complexing agent (acenaphthene) on the reaction rate.

RESULTS AND DISCUSSION

The product of the reaction of 3,5-NPA with pyridine is a betaine-like species (I) [2] which could not be isolated



(I)

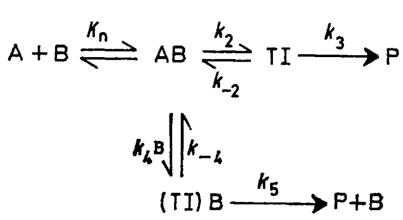
because of its highly hygroscopic nature. Monohydrated betaines, pyridinium hydrogen phthalates, formed from several different pyridines, were isolated and characterized by n.m.r. spectroscopy and *X*-ray diffraction.[3]

Table 1

Variation of k_{obs} with $[C_5H_5N]$ and with temperature in benzene; $[3,5\text{-NPA}] = 5 \times 10^{-4}$M

$10^2[C_5H_5N]$/M	10^2k_{obs}/min^{-1} 10°	20°	30°	50°
2·20	1·11	1·24	1·29	1·59
4·39	3·26	2·80	2·83	3·42
6·59	5·18	4·7	5·31	5·07
8·79	7·73	7·0	7·6	8·2
10·99	10·8	9·0	10·7	11·7
13·18	12·2	12·0	12·9	15·5
15·38	15·5	15·0	16·2	19·4
17·58	22·7	17·7	21·9	23·7
19·77	23·8			28·4

Table 1 shows the variation of the pseudo-first-order rate constant (in benzene) k_{obs} with the concentration of pyridine and with temperature (k_{obs} is defined as the rate constant obtained when the reaction order is degenerate with respect to pyridine). Scheme 1 explains the variation of k_{obs} with the concentration of pyridine. A Stands for anhydride, B for pyridine, AB for the *n*–π charge-transfer complex [1] formed between the



Scheme 1

two reagents (stability constant K_n), TI for the tetrahedral intermediate, and P for the product. The pseudo-first-order rate constant is given by equation (1)

$$k_{obs} = k_aK_n[C_5H_5N] + k_bK_n[C_5H_5N]^2/(1 + K_n[C_5H_5N]) \quad (1)$$

where $k_a = k_2k_3/(k_{-2} + k_3)$ and $k_b = k_4k_5/(k_{-4} + k_5)$ if TI is a steady-state concentration and AB accumulates. $[C_5H_5N]$ Is the concentration of pyridine, and $[C_5H_5N] \gg [3,5\text{-NPA}]$, the analytical concentration of anhydride.

A different situation was observed [2] previously in regard to the relative magnitudes of k_a, k_b, and K_n. In this case $K_n[C_5H_5N] \leqslant 1$ and equation (1) gave linear plots. Table 2 contains the activation parameters obtained from the variation of k_bK_n with temperature.

Table 2

Variation of the kinetic parameters with temperature and activation parameters for the reaction of 3,5-NPA with pyridine

t/°C	k_aK_n/l^2 mol^{-2} min^{-1}	k_bK_n/l^3 mol^{-3} min^{-1}
10	0·62	2·98
20	0·50	3·75
30	0·52	3·88
50	0·59	4·30

$\Delta H^‡_{cat} = 1·3$ kcal mol^{-1}, $\Delta S^‡_{cat} = -60$ cal mol^{-1} K^{-1}, $\Delta G^‡_{cat} = 19$ kcal mol^{-1}.

The enthalpy of activation is small and this indicates that the expression k_bK_n for the catalysed path is complex as deduced from the rate equation: $\Delta H^‡_{cat} = \Delta H^‡_b + \Delta H^0$, where $\Delta H^‡_{cat}$ is the apparent enthalpy of activation of the catalysed path, $\Delta H^‡_b$ is the true enthalpy of activation related to k_b, and ΔH^0 is the enthalpy of formation of the CT complex.

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† Part XII, J. B. Nagy, O. B. Nagy, and A. Bruylants, submitted for publication to *J. Phys. Chem.*

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[2] D. Mukana, J. B. Nagy, O. B. Nagy, and A. Bruylants, in preparation.

[3] Chr. Colpin, Memoire de Licence, U.C.L., Louvain, 1973.

We consider the CT complex formed between the anhydride and pyridine as a reaction intermediate by analogy with previous observations.[1,2]

Because of experimental uncertainties the activation parameter for the uncatalysed path (k_aK_n) could not be calculated. Nevertheless the corresponding activation enthalpy must be near zero, again showing the complexity of the kinetic expression.

Influence of Acenaphthene on the Reaction Rate of **3,5**-*NPA with Pyridine in Benzene.*—The rate of the reaction of tetrachlorophthalic anhydride with triethylamine in different solvents[4] is lowered by external complexing agents. The CT complexes formed between the donors and the anhydride are almost unreactive towards tertiary amines. In almost every reaction studied (there are only few exceptions[5]) the complexing agent inhibits the reaction.

In the present case acenaphthene was used as the complexing agent; $[C_{12}H_{10}]$ varied from 10^{-1} to 1M, $[C_5H_5N]$ from 0·07 to 0·3M. Table **3** gives the observed pseudo-first-order rate constants $k^D{}_{obs}$ in the presence of the acenaphthene.

TABLE 3

Variation of $k^D{}_{obs}$ with $[C_{12}H_{10}]$ and $[C_5H_5N]$ at 20° in benzene; [3,5-NPA] = 5 × 10^{-4}M

$[C_{12}H_{10}]$/M 0·1		0·3		0·5		0·7		1·0	
$10[C_5H_5N]$/M	$10k_{obs}$/ min^{-1}	$10[C_5H_5N]$/M	$10k_{obs}$/ min^{-1}	$10[C_5H_5N]$/M	$10k^D{}_{obs}$/ min^{-1}	$10[C_5H_5N]$/M	$10k^D{}_{obs}$/ min^{-1}	$10[C_5H_5N]$/M	$10k^D{}_{obs}$/ min^{-1}
1·043	0·76	1·043	0·65	0·693	0·37	1·052	0·52	1·066	0·46
1·391	1·15	1·391	1·05	1·035	0·62	1·403	0·78	1·421	0·66
1·738	1·66	1·738	1·41	1·381	0·89	1·753	0·99	1·776	0·89
2·086	1·93	2·086	1·77	1·726	1·13	2·104	1·42	2·131	1·18
2·434	2·62	2·434	2·03	2·071	1·66	2·455	1·82	2·487	1·51
2·761	3·38	2·761	2·74	2·805	2·38			2·842	1·96
P 0·45		0·42		0·42		0·35		0·28	
Q 2·75		2·08		1·60		1·50		1·40	

If we suppose that the π–π type complex formed by acenaphthene and 3,5-NPA does react, the kinetic results can be explained by Scheme 2. K_π Is the complexation constant of A with D (acenaphthene) and $K_{n\pi}$ is the complexation constant of AD with B, ABD being the ternary complex of A, B, and D.

Postulating steady-state conditions for all tetrahedral intermediates (pre-equilibrium for AB, AD, and ABD), the rate equation is given by equation (2) with

$$k^D{}_{obs} = \frac{(k_aK_n + k_cK_\pi K_{n\pi}[C_{12}H_{10}])[C_5H_5N]}{1 + K_\pi[C_{12}H_{10}]} + \frac{k_bK_n + k_dK_\pi K_{n\pi}[C_{12}H_{10}]}{1 + K_\pi[C_{12}H_{10}]}[C_5H_5N]^2 \qquad (2)$$

$k_c = k_6k_7/(k_{-6} + k_7)$ and $k_d = k_8k_9/(k_{-8} + k_9)$ and if $[C_{12}H_{10}] \gg$ [3,5-NPA] (the experimental conditions), $K_n[C_5H_5N] \ll 1$ [verified by equation (1)] and $K_{n\pi}K_\pi$ $[C_5H_5][C_{12}H_{10}] \ll 1$.

Supposing that equation (3) holds, equation (2) can be

$$k^D{}_{obs} = P[C_5H_5N] + Q[C_5H_5N]^2 \qquad (3)$$

linearized in the form (4) for the uncatalysed reaction,

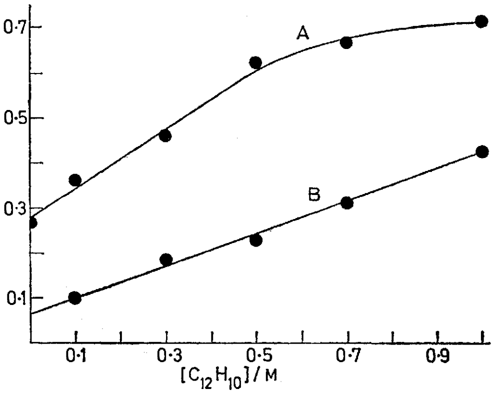
$$\frac{[C_{12}H_{10}]}{k_aK_n - P} = \frac{1}{k_aK_n - k_cK_{n\pi}} \cdot \frac{1}{K_\pi} + \frac{[C_{12}H_{10}]}{k_aK_n - k_cK_{n\pi}} \qquad (4)$$

and in the form (5) for the catalysed one. Similar expressions were first derived by Colter *et al.*[5]

$$\frac{[C_{12}H_{10}]}{k_bK_n - Q} = \frac{1}{k_bK_n - k_dK_{n\pi}} \cdot \frac{1}{K_\pi} + \frac{[C_{12}H_{10}]}{k_bK_n - k_dK_{n\pi}} \qquad (5)$$

The good linearity of the plot of $[C_{12}H_{10}]/(k_bK_n - Q)$ *vs.* $[C_{12}H_{10}]$ (Figure) yields $k_dK_{n\pi} = 1{\cdot}0$ l^3 mol^{-3} min^{-1} and $K_\pi = 5{\cdot}5$ l mol^{-1} at 20° (2·4 l mol^{-1} from spectrophotometric measurements[6]). The composition of the complex AD is 1 : 1 as determined by Liptay's matrix method.[7]

Because of the relatively great uncertainties in P, no parameters could be extracted from equation (4).



Effect of external complexing agent (acenaphthene) on the reaction of 3,5-dinitrophthalic anhydride with pyridine: A, plot of Q^{-1} against $[C_{12}H_{10}]$; B, plot of $[C_{12}H_{10}]/(k_bK_n - Q)$ against $[C_{12}H_{10}]$

If we suppose that the complex AD does not react [$k_c = k_d = 0$ in equation (2)] we have equation (6). The

$$\frac{1}{Q} = \frac{1}{k_bK_n} + \frac{K_\pi}{k_bK_n}[C_{12}H_{10}] \qquad (6)$$

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[4] J. B. Nagy, O. B. Nagy, and A. Bruylants, *J.C.S. Perkin II*, 1972, 2084.

[5] A. K. Colter and S. S. Wang, *J. Amer. Chem. Soc.*, 1963, **85**, 114; A. K. Colter, S. S. Wang, G. H. Megerle, and P. S. Ossip, *ibid.*, 1964, **86**, 3106.

[6] S. Dupire, Memoire de Licence, U.C.L., Louvain, 1971.

[7] G. Briegleb, 'Elektronen Donator-Acceptor Komplexe,' Springer Verlag, Berlin, 1961.

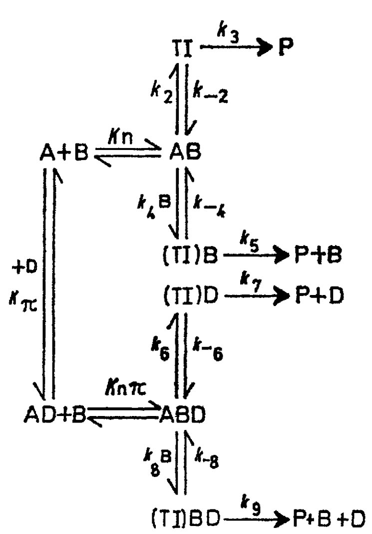
Figure also shows the variation of $1/Q$ with $[C_{12}H_{10}]$. It can be seen that the experimental points do not fall on a straight line. This means that the complex AD does react, *i.e.* it is an intermediate. Only in very few cases could the reactivity of the CT complex formed by the reactant and the external complexing agent be verified.[8,9]

TABLE 4

Variation of k^D_{obs} with temperature and the activation parameters in benzene [3,5-NPA] = 5×10^{-4}M, $[C_{12}H_{10}]$ = 1·0M

10°		30°	
$10[C_5H_5N]$/M	$10^2k^D_{obs}$/min^{-1}	$10[C_5H_5N]$/M	$10^2k^D_{obs}$/min^{-1}
0·659	2·74	0·47	2·88
0·879	3·84	0·705	4·34
1·099	4·58	0·94	6·1
1·318	5·7	1·175	8·6
1·538	6·67	1·41	11·9
1·758	8·1	1·645	15·0
1·977	9·5	1·88	17·3
P	0·38		0·38
Q	0·45		3·05

$\Delta H^\ddagger_{cat}$ = 15·7 kcal mol^{-1}, $\Delta S^\ddagger_{cat}$ = −15 cal mol^{-1} K^{-1}, $\Delta G^\ddagger_{cat}$ = 19·7 kcal mol^{-1} at 20°.



SCHEME 2

Table 4 shows the variation of k^D_{obs} with temperature ($[C_{12}H_{10}]$ = 1M). Once again the catalysed path (Q) is much more sensitive to the temperature than the uncatalysed path (P). The apparent inhibitory effect of acenaphthene decreases with increasing temperature: k^D_{obs}/k_{obs} = 0·36 at 10°; 0·50 at 20°, and 0·68 at 30°. This may be due to the decrease of K_π when the temperature increases (ΔH^0 = −4·3 kcal mol^{-1}).[6]

Solvent Effects on the Reaction of 3,5-*NPA with Pyridine*.—Table 5 shows the variation of k_{obs} with $[C_5H_5N]$ in different solvents at 20°. There is no correlation between log k_aK_n (or log k_bK_n) and the polarity–polarisability parameter S_M[1,10] (or Z[11]). This also shows that the quantities k_aK_n and k_bK_n are complex values and K_n should be determined whenever possible before variations in the true kinetic constants k_a and k_b are interpreted.

The present study agrees with our previous results.[4] The rate of the reaction of 3,5-dinitrophthalic anhydride is lowered in the presence of an external complexing agent: k^D_{obs}/k_{obs} = 0·5 at 20° ($[C_5H_5N]$ = 0·17M, $[C_{12}H_{10}]$ = 0·5M). The 50% rate decrease is only apparent. Detailed kinetic analysis shows that the complex substrate–external donor does react, retaining 27% ($k_dK_{n\pi}/k_bK_n$ = 0·27) of the reactivity of uncomplexed substrate. Therefore simple comparisons of pseudo-first-order rate constants (which are quite frequent [8]) do not lead to a correct view of the phenomenon.

TABLE 5

Variation of k_{obs} with $[C_5H_5N]$ and the kinetic parameter in different solvents at 20°; [3,5-NPA] = 5×10^{-4}M

Toluene		p-Xylene		Mesitylene	
$10[C_5H_5N]$/ M	10^2k_{obs}/ min^{-1}	$10[C_5H_5N]$/ M	10^2k_{obs}/ min^{-1}	$10[C_5H_5N]$/ M	10^3k_{obs}/ min^{-1}
0·607	3·9	0·844	3·2	0·391	1·36
0·809	5·75	1·267	5·6	0·781	2·37
1·011	7·26	1·689	8·8	1·172	5·1
1·213	9·8	2·111	12·2	1·563	8·5
1·416	12·3	2·533	15·3	1·953	12·2
1·618	14·4	2·956	20·4	2·344	17·4
		3·378	23·7	2·734	19·8
				3·125	28·3
				3·516	33·4
k_aK_n	0·50	0·23		0·22	
k_bK_n	2·5	1·22		2·07	

EXPERIMENTAL

3,5-Dinitrophthalic anhydride was obtained from the corresponding diacid by dehydration in acetic anhydride, m.p. 163·3°, and was handled under nitrogen. The diacid, m.p. 226°, was synthetized from the 3,5-dinitrotoluic acid by oxidation with nitric acid (d = 1·15) in a sealed tube at 143°. Acenaphthene (Fluka) was recrystallized five times from aqueous ethanol, m.p. 95—96°. Pyridine (UCB) was refluxed over NaOH and distilled under nitrogen. Solvents were purified by standard methods and were dried over molecular sieves.

Measurements.—The rate of reaction was determined by following the disappearance of the 3,5-NPA band at 29·25 kK with a Unicam SP 800 spectrophotometer, the temperature being maintained constant to 0·1°.

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[10] J. C. Jungers and L. Sajus, ' L'analyse Cinétique de la Transformation Chimique,' Technip, Paris, 1968, 1st edn., vol. II.

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