Solvent Effects upon the Rates of Acid-induced Decomposition of 3-Methyl-1-*p*-tolyltriazene and Diphenyldiazomethane

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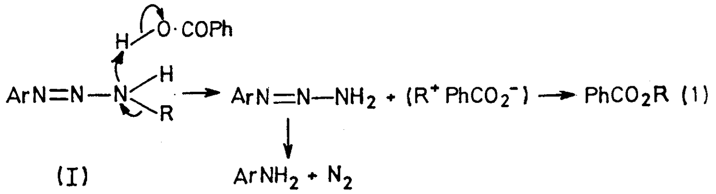
Rates of reaction of 3-methyl-1-*p*-tolyltriazene with benzoic acid to form methyl benzoate, *p*-toluidine, and nitrogen have been measured in a wide variety of aprotic solvents. Similar studies are also reported on the reactions of diphenyldiazomethane with benzoic acid and with *p*-nitrophenol. Large solvent effects upon all reactions are observed; those of the triazene correlate well with the donor character of the solvent as expressed by several empirical parameters. The reactions of diphenyldiazomethane appear to be better interpreted by a multiple correlation with both donor and polar (electrostatic) contributions to the solvent effect.

In the preceding paper [1] we described the mechanism of the carboxylic acid-induced decomposition of alkylaryltriazenes (I) in terms of a concerted electrophilic displacement of a carbonium ion by a proton at nitrogen [reaction (1)]. This is one example of a small number of reactions initiated by a proton transfer taking place in the rate-determining step, and which will readily occur in an aprotic solvent. It was therefore of interest to compare reaction rates in a wide variety of solvents in order to clarify the solvent parameters which are relevant to this process. It was also of interest to compare the solvent effects on the triazene decomposition with those of the analogous reaction of diphenyldiazomethane (DDM) for which a considerable amount of data is available [2] and which was extended by the present study.



EXPERIMENTAL

3-Methyl-1-*p*-tolyltriazene was prepared as described.[1] Solvents were purified by standard methods and stored under nitrogen. Diphenyldiazomethane was prepared by the method of Schroeder and Katz [3] and solutions stored at 4°. The carboxylic acids and phenols used were purified by recrystallisation to constant m.p. which agreed with literature values. The reactions were followed by spectrophotometry using a thermostatted cell within a Unicam SP 1800 spectrophotometer.

RESULTS AND DISCUSSION

Satisfactory second-order rate constants were obtained for the reactions of (I) with benzoic acid in fifteen aprotic solvents of varied character.[1] The values did not appear to be very sensitive to the acid concentrations over the range used (10^{-2}—10^{-3}M), the initial triazene concentrations being similar. Diphenyldiazomethane reactions, being much slower, were studied under conditions such that the acid was some 10-fold in excess when pseudo-first-order conditions prevailed. The rate constants observed were rather dependent upon the benzoic acid concentration used which was standardised at 0·1M for comparison purposes. The arguments presented here are not greatly affected by this variation which has been shown to be due to different reactivity attributable to monomeric and dimeric forms of the carboxylic acid.[4] That this is the case is shown by the parallel results obtained using nitrophenols as the acids which are not

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[1] N. S. Isaacs and E. Rannala, preceding paper.

[2] (*a*) R. A. More O'Ferrall, W. K. Kwok, and S. I. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 5553; (*b*) A. Buckley, N. B. Chapman, M. J. R. Dack, J. Shorter, and H. M. Wall, *J. Chem. Soc.* (*B*), 1965, 631; (*c*) A. Buckley, N. B. Chapman, and J. Shorter, *ibid.*, 1968, 195; (*d*) N. B. Chapman, J. R. Lee, and J. Shorter, *ibid.*, 1969, 769; 1970, 755; (*e*) N. B. Chapman, M. R. J. Dack, and J. Shorter, *ibid.*, 1971, 834.

[3] W. Schroeder and L. Katz, *J. Org. Chem.*, 1954, **19**, 718.

[4] N. B. Chapman, A. Ehsan, J. Shorter, and K. J. Toyne, *Tetrahedron Letters*, 1968, 1049.

subject to dimerisation. Measured rate constants are given in Tables 1 and 2.

TABLE 1

Rate coefficients for reactions of 3-methyl-1-*p*-tolyltriazene or DDM with benzoic acid in aprotic solvents at 30°

	Solvent parameters			Reactions		
Solvent	E_T [a]	DN [b]	10^3M_{50} [c]	A [d]	B [e]	C [f]
Nitromethane	46·3	2·7		0·790	3·57	(10)
Dichloromethane	41·1	4	0·66	0·337	6·10	4·84
Chloroform	39·1	4	3·2	0·267	1·73	4·014
Nitrobenzene	42·0	4·4		0·236		
Chlorobenzene	37·5					4·65
Benzene	34·5	6	1·9	0·083	2·95	4·53
Toluene	33·9					3·42
Mesitylene						2·38
Cyclohexene	33·5		6·2			2·96
Benzonitrile	42·0	11·9		0·11		
Acetonitrile	46·0	14·1	3·6	0·103		0·817
Ethyl acetate	38·1	17·1	380	0·00785		0·0926
Acetone	42·2	17·0	35	0·00864	0·084	0·0687
1,4-Dioxan	36·0	15·0		0·00310		0·0223
Diethyl ether	34·6	19·2	2300	0·0011		0·0103
Tetrahydrofuran	37·4	20·0		0·00057	0·010	0·0151
Dimethyl sulphoxide	45·0	29·8		0·00122	0·050	0·0010
Hexamethylphosphoramide		38·8		Very slow		Very slow

[a] Ref. 6. [b] Ref. 7. [c] $10^3 \times$ molarity of CF_3CO_2H needed to cause 50% protonation of *p*-dimethylaminoazobenzene (10^{-4}—10^{-5}M) in the appropriate solvent. [d] k_1 (min^{-1}) for $Ph_2CN_2 + PhCO_2H \longrightarrow Ph_2CHOCOPh + N_2$. [e] 10^3 k_1 (min^{-1}) for Ph_2CN_2 + *p*-$NO_2C_6H_4OH \longrightarrow Ph_2CHOC_6H_4NO_2$-*p*. [f] k_2 (l mol^{-1} min^{-1}) for *p*-$MeC_6H_4N{=}N{-}NHMe + PhCO_2H \longrightarrow$ *p*-$MeC_6H_4NH_2 + N_2 + PhCO_2Me$.

Reactions rates of the triazene decompositions are markedly affected by the nature of the solvent and increase some 10^4-fold between dimethyl sulphoxide and nitromethane. In attempting an explanation of the solvent effects one must compare the kinetic data with relevant physical properties of the solvent or with the experimental effects of the same solvents upon other chemical processes. Solvent polarity, the ability of a solvent to interact with ions, may be measured as a function of the dielectric constant ε, usually as the Kirkwood [5] function $(\varepsilon - 1)/(2\varepsilon + 1)$, or by means of empirical scales such as the E_T scale of Dimroth *et al.*[6] based on solvatochromism. With neither of these types of measure is there any correlation with the present rate data (Table 3).

TABLE 2

Arrhenius parameters for the reaction of 3-methyl-1-*p*-tolyltriazene with benzoic acid in several solvents

Solvent	T/K	k_2/ l mol^{-1} min^{-1}	E_A/ kJ mol^{-1}	log A
Chloroform	313	8·526	48·3	7·23
	308	5·634		
	303	4·014		
	298	2·970		
	293	1·986		
Benzene	313	6·828	41·4	5·64
	308	5·844		
	303	4·530		
	293	2·149		
Acetone	313	0·155	46·0	5·06
	308	0·101		
	303	0·0687		
	293	0·0359		

For a rate-determining proton transfer, the solvent effect might be supposed to be related to the basicity or donor properties of the medium. There are a number of empirical measures which depend more or less on this property and include the donor number, DN, of Gutmann [7] (the enthalpy of co-ordination of the solvent molecule to $SbCl_5$ in dichloroethane solution), the Taft [8] *P* scale (obtained from fluorine n.m.r. chemical shifts upon *p*-fluoronitrosobenzene and responding, apparently, to both donor and acceptor properties of the medium), heats of mixing of solvent with chloroform, Q_m,[9] and the change in O–D stretching frequency $\Delta\nu_D$ of CH_3OD in a given solvent referred to solvent benzene.[10] To this we have added a new scale more closely related to proton transfer phenomena, M_{50}, defined as the concentration of trifluoroacetic acid in the given solvent required to cause 50% protonation of *p*-dimethylaminoazobenzene, a nitrogen base with visible indicator properties. Neutralisation curves were plotted by spectrophotometric determination of the indicator ratio and are illustrated in the Figure.

Correlation analyses have been carried out between the rates of reaction and the various solvent parameters both singly and in combination since it is quite probable that the solvent manifests both ion-stabilising (' polar ') and donor effects upon the reaction. Values of the single and multiple correlation coefficients *r* thus obtained are set out in Table **3**. Similar analyses have also been given and are here extended for the reactions of diphenyldiazomethane both with benzoic acid and with *p*-nitrophenol.

In all these reactions, the strongest correlation with a

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[5] J. G. Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351.

[6] K. Dimroth, C. Reichardt, T. Siepmann, and E. Bohlmann, *Annalen*, 1963, **661**, 1.

[7] V. Gutmann and E. Wychera, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 257; V. Gutmann, *Co-ordination Chem. Rev.*, 1967, **2**, 239.

[8] R. Taft quoted by C. D. Richie, ' Solute–Solvent Interactions,' eds. J. F. Coetzee and C. D. Richie, Dekker, New York, 1969.

[9] E. Arnett, *Progr. Phys. Org. Chem.*, 1963, **1**, 223.

[10] T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Japan*, 1968, **41**, 767.

TABLE 3

Single and multiple correlation coefficients r for the effects of aprotic solvents upon reaction rates

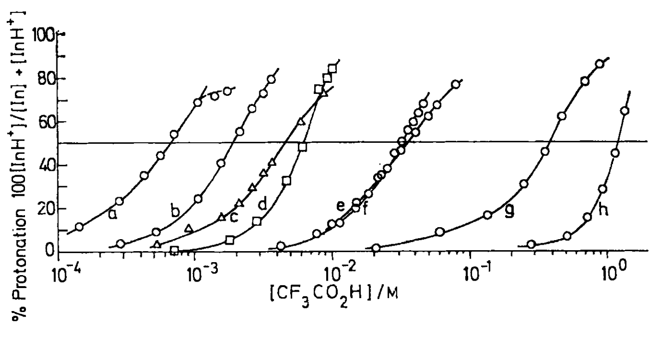
Correlation with Reaction	DN	E_T	Q_m	P	M_{50}	DN + E_T	P + E_T
A[a]	0·9006	0·0875	0·9141	0·4791	0·9252	0·9700	
B[a]	0·8087	0·0461	0·9065			0·8168	
C[a]	0·9740	0·0053	0·9624	0·1856		0·9739	0·1885
D[b]	0·9132	0·1237				0·9593	

[a] See Table 1. [b] Data from ref. 2*e*.

single solvent parameter is found with values of DN, which seems to be the best measure of the donor capabilities of the solvent. Good fits were also noted with Q_m and with M_{50} which have a similar physical basis but not with the P or $\Delta\nu_D$ scales which appear to depend upon other solvent functions including hydrogen bonding capabilities.[11] The regression equation for the relationship between rates of triazene decomposition and DN may be expressed as (2). No improvement on this was

$$\log k = 1{\cdot}278 - 0{\cdot}1437\ \mathrm{DN} \quad (r\ 0{\cdot}974) \quad (2)$$

found by attempting a two parameter correlation, *e.g.* using DN and E_T. On the other hand, all the diphenyldiazomethane rates showed an improved correlation when a polar term was added. The regression equation determined for reactions of DDM with benzoic acid under pseudo-first order conditions took the form (3).



Neutralisation curves for *p*-dimethylaminoazobenzene (In) by trifluoroacetic acid in various solvents: a, CH_2Cl_2; b, C_6H_6; c, MeCN; d, cyclohexene; e, $CHCl_3$; f, Me_2CO; g; EtOAc; h, Et_2O.

$$\log k = -4{\cdot}297 - 0{\cdot}119\ \mathrm{DN} + 0{\cdot}105\ E_T \quad (r\ 0{\cdot}970) \quad (3)$$

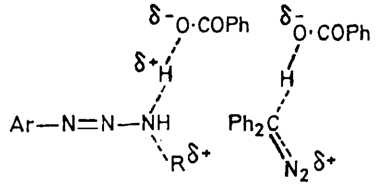
This equation compares with the two-parameter correlation (4) determined for the same reaction (under second-order conditions) in which the donor scale used was Q_m and the polar scale a function of dielectric constant f(ε).[2e] Thus while the solvent donor properties appear

$$\log k = -0{\cdot}050 - 0{\cdot}00337\ Q_m + 1{\cdot}481\ \mathrm{f}(\varepsilon) \quad (r\ 0{\cdot}924) \quad (4)$$

to be the most significant term for both triazene and DDM reactions, there is a difference in that the former is insensitive to polar effects while the latter shows some response to this property. This is explicable if we postulate the two transition states as (II) and (III) respectively, *i.e.* a much greater dipole moment in the latter, corresponding to a greater extent of proton transfer.

Two ways in which the medium might affect the proton-donating capabilities of benzoic acid may be considered. The basicity of the solvent would determine the extent of interaction, through hydrogen-bonding, between it and the acid, strong hydrogen bonds presumably reducing the apparent acidity while other factors less well understood affect the carboxylic acid monomer–dimer equilibrium. The latter is known to be of importance in the reactions of DDM, the dimer being the more reactive form so that measured rate constants increase with increasing benzoic acid concentration. We have confirmed that this is the case and for that reason have included studies using nitrophenols which are not subject to dimerisation, in order to exclude the possibility that carboxylic acid association can alone account for the observed solvent effects. The observed rate constants did not sensibly change over the rather limited range of benzoic acid concentrations used in reactions of the triazenes though it would be expected that in a solvent such as benzene the effect of dimerisation would be apparent if a sufficiently wide range of acid concentrations were spanned.

We conclude that the major effect of an aprotic medium lies in its basicity. This would accord with the observation that rate changes are predominantly attributable to changes in the pre-exponential factor while activation energies do not greatly change (Table 2). This could indicate attack of the triazene by an increasingly solvated carboxylic acid in the series chloroform, benzene, acetone.



(II) (III)

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[11] I. A. Koppel and V. A. Palm, 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, New York, 1972.