Substituent Effects in the Reaction of Triphenylphosphine with Diazodiphenylmethane: the Interpretation of a U-Shaped Hammett Correlation in an Elementary Biphilic Reaction

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The reaction between diazodiarylmethanes and triphenylphosphine has previously been shown to be an elementary biphilic reaction in which each reactant behaves simultaneously as both electrophile and nucleophile. Frontier molecular orbital considerations provide a basis for relating structure and reactivity. Diazodiphenylmethane, however, is an order of magnitude more reactive than expected, and substituents in the phenyl groups of the diazoalkane enhance the reaction rate, whether they are electron-withdrawing or electron-releasing, giving rise to a U-shaped Hammett correlation. Evidence is now presented that the substituent effect cannot arise from disturbance of simple energy matching of the frontier molecular orbitals of the two reactants, but rather results from conformational changes in the diazo-compound on passing from the reactant to the transition state. This evidence comprises (*i*) the linearity of Hammett plots for the effects of substituents in triphenylphosphine on the reactivity towards diazodiphenylmethane, and (*ii*) a comparison of the reactivity of diazodiphenylmethanes bearing two substituents of opposite polar effect when these are present in the same and in different aromatic groups.

In an earlier publication[1] we described observations on structure and reactivity in the reaction of a group of diazodiarylmethanes with triphenylphosphine in acetonitrile solution, reactions that lead to the binding of the phosphorus atom to the terminal nitrogen of the diazo-compound forming a so-called phosphazine (sometimes referred to as a phosphinazine). Although this reaction can be formulated as a simple coordination of a nucleophilic centre on phosphorus to an electrophilic centre on nitrogen (eqn. 1),[2] the observed effect on the reaction rate of structural variations in the diazo-compound were in the opposite direction to predictions made on that basis and were rather small. Thus, for example, 9-diazofluorene **1** the central ring of which might be expected to become associated in the transition state with a favourable arrangement of six π-electrons had a second-order rate constant k_2, only about one seventh of that of the diazodibenzocycloheptatriene **2** which would acquire a less favourable eight π-electrons. The reaction thus has the general character of an elementary (*i.e.*, single step) biphilic reaction[3] in which both the diazoalkane and the phosphine simultaneously behave as electrophile and nucleophile, thereby modifying the build-up of π-electron density in the diazo-moiety. It was further shown that the structure of the diazoalkane could be correlated with its reactivity by consideration of the computed energy separations of the frontier molecular orbitals, the HOMO and LUMO of the two reactant molecules. Diazodiphenylmethane **3**, however, deviated from the correlation, showing a value of k_2 that was some ten times larger than would have been predicted. Moreover, *p*-substituents in the diazo-compound, whether electron-releasing such as methoxy or electron-withdrawing such as chloro, caused an increase in k_2 and hence a concave U-shaped Hammett correlation.

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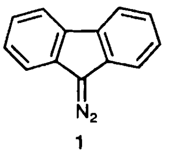

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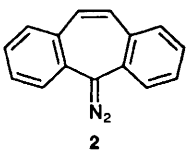

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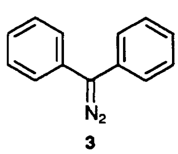

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Of the several interpretations of U-shaped Hammett correlations,[4] an attractive possibility is an adaptation (shown in Fig. 1) of Klumpp's treatment of substituent effects in the reaction of 3,5-dichloro-2,4,6-trimethylbenzonitrile oxide with substituted phenylacetylenes.[5] In Fig. 1, the substituent is represented as interacting with the frontier orbitals of one reactant, thereby raising the energies of both its HOMO and LUMO with an electron-releasing group (ERS) or lowering their energy with an electron-withdrawing group (EWS). If the energies of the HOMOs and LUMOs of the two reactants are matched in the case of the unsubstituted compound so that the two HOMO–LUMO interactions are equally important, then substituents of either polarity will lead to a stronger frontier orbital interaction as the energy separation of one HOMO–LUMO pair is decreased and becomes dominant.

Such an interpretation was not considered at the time on the basis that FMO theory failed to predict satisfactorily the

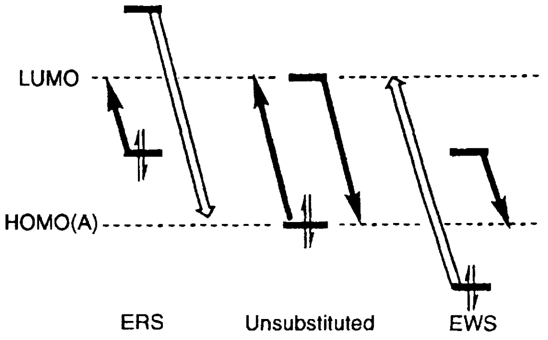

Fig. 1 Schematic frontier orbital energy diagram showing how, given HOMO–LUMO energy matching in the unsubstituted case, an electron releasing-substituent (ERS) can lead to a dominant LUMO(A)–HOMO(B) interaction whereas an electron-withdrawing substituent (EWS) leads to a dominant HOMO(A)–LUMO(B) interaction (filled arrows show the dominant interactions)

Table 1 Average second-order rate constants for the reaction of substituted diazodiphenylmethanes with triphenylphosphine in acetonitrile at 30 °C

Substituents	$k_2/10^{-4}$ dm^3 mol^{-1} s^{-1}
H	$31._9$
4,4'-$(CH_3)_2$	$32._1$
3-NO_2-4-CH_3	15_9
3-NO_2-4'-CH_3	27_9
3,3'-$(NO_2)_2$	84_5

Table 2 Second-order rate constants for the reaction of diazodiphenylmethane with monosubstituted triphenylphosphines in acetonitrile at 30 °C

Substituents	$k_2/10^{-4}$ dm^3 mol^{-1} s^{-1}
H	$32._8$
4-OCH_3	$44._1$
4-Cl	$26._4$
3-CF_3	$16._9$

reactivity of **3** with triphenylphosphine and could not therefore be expected to deal with the substituent effects.[1] Instead the view was taken that the U-shaped Hammett plots could be attributed to the fact that **3** was the only diazoalkane in the group examined in which the orientation of the aryl groups was unrestricted by fusion to a ring carrying the diazo-functionality. In consequence, in the transition state, the conformation of the rings with respect to the plane containing the diazo-group would be free to adjust itself so as to minimise the free energy, the adjustment varying according to the substituent in the ring. Thus the frontier orbital energy calculated on the basis of the isolated reactant could be quite inappropriate as a guide to the strength of the interaction of the corresponding orbitals with the frontier orbitals of the phosphine.

Direct evidence in support of this interpretation was not available although our subsequent determination[6] of the crystal structures of three of the phosphazines studied kinetically showed that the one from **3** did indeed show a substantial change in the orientation of the aromatic rings relative to the reactant; the phenyl groups were found to be almost orthogonal to each other, consistent with the idea that, in the transition state, one phenyl group was conjugated with the allyl-type π-system of the diazo-function (the HOMO of the diazoalkane) and the other homoconjugated with the in-plane N–N π-system (the LUMO), as envisaged by the conformational change interpretation. Additionally it was known that, in the reaction of **1** with triphenylphosphine, substituents in either the diazoalkane[7] or the phosphine[8] gave simple Hammett behaviour (ρ = *ca.* 2.2 and −1.0, respectively). In 9-diazofluorene the aromatic rings are known from crystallographic evidence[9] to be conjugated with the allyl-type orbitals of the diazo-group and the same interaction is retained in the phosphazine product.[6]

We now report further experiments aimed at confirming our earlier interpretation of substituent effects in diazodiphenylmethane. To this end we have investigated the kinetic effect of additional substituents in the diazo-compound on the reaction with triphenylphosphine, in particular the effect of having two substituent groups of opposite polar effect in the same ring and in different rings. We have also examined substituents in triphenylphosphine and their effect on the rate of the reaction with **3**; the conformation of the aryl rings in the phosphine is not expected to influence the energies of its frontier orbitals and normal Hammett-type correlations would be expected. However, if the previously observed curvature in Hammett plots were the result of the substituents' disturbing a matching of frontier orbital energies in the two reactants as in Fig. 1, then substituents in the phosphine should also give rise to a U-shaped Hammett plot.

Results

Effects of Combinations of Substituents in Diazodiphenylmethane.—In an attempt to address directly the question of whether the two rings in **3** interact independently with the reaction centre as the transition state is reached, we have compared the reactivity of two isomeric diazodiphenylmethanes, one with a 3-nitro and a 4-methyl substituent in the same phenyl group and the other with the substituents in different rings. Values of the second-order rate constant, k_2 ($= -[PPh_3]^{-1}d\ln[Ar_2CN_2]/dt$), averaged over determinations at two different large excesses of the phosphine, are in Table 1 together with results on the 3,3'-dinitro- and 3,3'-dimethyl analogues.

The Reaction of Diazodiphenylmethane with Substituted Triphenylphosphines.—A series of triphenylphosphines carrying a single substituent in one of the aromatic rings was prepared by reaction of a Grignard reagent with chlorodiphenylphosphine in ether at 0 °C. Such reactions are known to be highly susceptible to oxidation of the product to the phosphine oxide, but, by carrying out the initial part of the work-up under nitrogen, it proved possible to obtain the required phosphines, the oxidation state of phosphorus being confirmed by the observed ^{31}P chemical shift. Rates of reaction of the phosphines towards diazodiphenylmethane (0.005 mol dm^{-3}) were determined spectrophotometrically (526 nm) in acetonitrile using the phosphine in ten- or twenty-fold excess. Values of the second-order rate constant from reactions are in Table 2; individual values from experiments at different triphenylphosphine concentrations differed from the mean by no more than 5%.

Treatment of these data using the Hammett equation gives an acceptable linear correlation over the range of substituents examined; the reaction constant, ρ, is −0.58 (r = 0.978).

Discussion

U-*Shaped Hammett Correlations.*—FMO theory incorporates a duality of substituent interaction with the reaction centre *via* the HOMO and LUMO and thus appears to lend itself to the interpretation of cases of U-shaped Hammett plots in elementary biphilic processes. As indicated schematically in Fig. 1, however, substituents in one reactant are taken to change the frontier orbital energies in the same sense, which is likely to be the case when both the HOMO and LUMO have similar symmetry. In diazoalkanes, the frontier orbitals are thought to be of different symmetry,[1] the HOMO being a filled allyl-type π-orbital (B_1 in C_{2v}) while the LUMO is the in-plane π-orbital between the N atoms (B_2 in C_{2v}) and in consequence substituents in an aromatic ring attached to the diazo-carbon atom will interact with these orbitals in ways that are different and depend on the conformation of the aryl groups. Thus it is expected that substituted phenyl groups in 9-diazofluorene will interact most strongly by conjugation with the HOMO. Substituted phenyl groups in diazodiphenylmethane, on the other hand, where conformational change is possible, may interact with either the HOMO or the LUMO (by homoconjugation).[10] Indeed, with different substituents in the two rings, the energies of the HOMO and LUMO could change in opposite directions.

Substituents in Diazodiphenylmethane.—The data in Table 1

Table 3 New compounds synthesised in the preparation of substituted diazodiphenylmethanes

			Analysis (%)					
			Found			Required		
Substituents	Compound	M.p./°C	C	H	N	C	H	N
3,3'-$(NO_2)_2$	diazo	124–126	54.5	2.8	19.4	54.93	2.84	19.71
4-CH_3,3'-NO_2	hydrazone	141–144	65.95	5.15	16.55	65.87	5.15	16.54
	diazo	77–80	66.4	4.35	16.6	66.39	4.38	16.59
4-CH_3,3-NO_2	hydrazone	oil	n.d.[a]	n.d.	n.d.	65.87	5.15	16.54
	diazo	65–73	66.5	4.45	16.3	66.39	4.38	16.59

[a] Not determined.

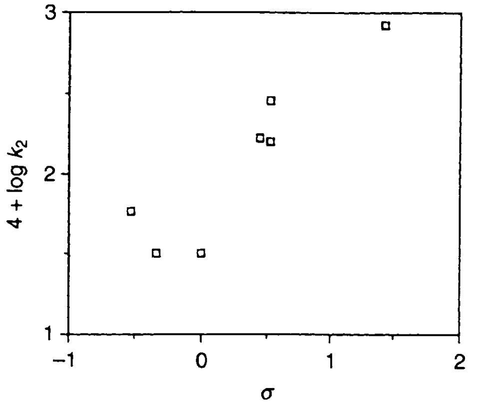

Fig. 2 Hammett plot for the reaction of substituted diazodiphenylmethanes with triphenylphosphine in acetonitrile at 30 °C

have been combined with our previously published results, averaging the values of k_2 where appropriate, to produce the U-shaped plot in Fig. 2. The new results extend one arm of the U-shape. There is a small but significantly increased reactivity for the compound having the methyl and nitro groups in different aromatic rings compared with the compound with both substituents in the same ring. Although the difference is in the expected sense, it cannot be claimed to validate unambiguously the idea that the duality of interaction of the substituents that is possible in the former compound is responsible. Intuitively a larger difference in reactivity might have been expected. In any case, the proximity of the substituents in the 3,4-disubstituted ring will enforce a rotation of the nitro-group out of the plane of the aromatic ring,[11] so that the compound may not be a suitable standard against which to compare the reactivity of the 3-nitro-4'-methyl isomer in which the nitro-group can adopt a conformation coplanar with the ring to which it is attached. On the basis of this evidence, the question of the dual interaction of the aryl groups with the developing P=N linkage in the transition state must remain open.

Reactivity of Substituted Triphenylphosphines with Diazodiphenylmethane.—The effect of substituents in triphenylphosphine on the reactivity towards diazodiphenylmethane is quite small, and the ρ-value, although it is based on a small data set, is only around half of that observed in the reaction with 9-diazofluorene, while still showing that the nucleophilic character of the phosphine is more important than its acceptor properties in the reaction with **3**. The most significant feature of the results, however, is that, over a range of substituents spanning strong conjugative electron-release to powerful inductive electron-withdrawal, the kinetic data show no sign of significant deviation from linearity in the Hammett plot. Since the Klumpp-type interpretation of the U-shaped Hammett correlation of the effect of substituents in the diazoalkane in terms of frontier orbital energy matching in the unsubstituted compound (Fig. 1) does not specify which of reactants A and B is the diazo-compound and which the phosphine, then substituents in the phosphine should also give rise to a U-shaped correlation. That they do not indicates that the simple interpretation in terms of frontier orbital energies is inadequate, and that substituents in the diazoalkane give rise to a more complicated pattern of behaviour. This arises as a result of a duality of the substituents' modes of interaction with the seat of reaction in the transition state *via* orbitals of different symmetry, coupled with conformational changes in passing from reactant to transition state that invalidate the application of simple FMO theory. We believe that our earlier interpretation is vindicated.

Experimental

Substituted Diazodiphenylmethanes.—All compounds were prepared by standard procedures used previously, involving the oxidation of the corresponding hydrazone (prepared by treatment of the ketone with an excess of hydrazine hydrate in ethanol solution) using yellow mercuric oxide in conjunction with a desiccating agent, usually sodium sulfate. Details of the new compounds are in Table 3. The purity of known diazoalkanes was confirmed by elemental analysis. All compounds showed satisfactory NMR and IR spectroscopic features.

Substituted Triphenylphosphines.—These compounds were prepared by the addition at 0 °C of ethereal chlorodiphenylphosphine to an excess of the appropriately substituted phenylmagnesium iodide, following literature procedures.[12] Reaction mixtures were worked up by being poured into aqueous ammonium chloride that had been deoxygenated by saturation with nitrogen. Column chromatography was on silica (eluent 4:1 v/v cyclohexane–toluene) followed by recrystallisation. Characterisation of all products was by elemental analysis and mass spectrometry, coupled with ^{31}P NMR spectroscopy. Results are given in Table 4. Attempts to prepare 4-methyltriphenylphosphine by the same procedure, in our hands, gave only the corresponding phosphine oxide.

Although the product phosphazines were isolated from the reaction mixtures, those derived from the reaction of **3** with the substituted phosphines and from triphenylphosphine with the methyl-nitro-substituted analogues of **3** were obtained as oils and were not further characterised.

Kinetics.—Reactions were followed spectrophotometrically at the wavelength of maximum absorbance of the diazo-compound in the visible region typically on solutions that were

Table 4 Substituted triphenylphosphines

		Analysis (%)				
		Found		Required		
Substituent	M.p./°C	C	H	C	H	δ_P[a]
4-CH_3O	76–78	78.1	5.9	78.07	5.86	−6.49
4-Cl	44–46	72.6	4.75	72.86	4.76	−6.25
3-CF_3	oil	68.6	4.25	69.09	4.27	−4.55

[a] Relative to phosphoric acid; for triphenylphosphine, δ_P is −4.87 and for triphenylphosphine oxide +30.01.

0.005 mol dm^{-3} in the diazo-compound and with a ten- and twenty-fold excess of the triarylphosphine.

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