

$C_{14}H_{16}O_2S$  requires M 248.09.

**Quenching of Anion 16 or 17 with 1-Bromopropane. 5-endo-(Phenylsulfonyl)-5-exo-n-propylbicyclo[2.2.1]hept-2-ene (19a):** white prisms; mp 65–66 °C (from ethyl acetate/pentane);  $^1H$  NMR ( $CDCl_3$ , TMS)  $\delta$  7.79–7.17 (m, 5 H, Ph–), 6.23 (dd, 1 H,  $J = 3.3, 2.5$  Hz, olefinic H-3), 6.16 (dd, 1 H,  $J = 3.3, 2.5$  Hz olefinic H-2), 3.09 (s, 1 H, bridgehead H-4), 2.87 (s, 1 H, bridgehead H-1), 2.00 (dd, 1 H,  $J = 12.8, 2.2$  Hz, H-6 endo) 1.60–1.20 (m, 7 H), 0.60 (t, 3 H,  $J = 7.2$  Hz, Me–);  $^{13}C$  NMR ( $CDCl_3$ ) 140.2, 138.4, 134.4, 133.4, 129.3, 129.1, 74.2, 49.2, 48.5, 43.2, 41.1, 37.7, 18.2, 14.8; IR (KBr) 3037, 2960, 1589, 1452, 1287, 1147, 1089; MS,  $m/z$  (%) 211 (10.5), 134 (17.2), 105 (34.5), 92 (20.1), 91 (59.9), 79 (26.5), 78 (21.3), 77 (29.6), 66 (100), 65 (28.2), 64 (26.4). Anal. Calcd for  $C_{16}H_{20}O_2S$ : C, 69.53; H, 7.29. Found: C, 69.51; H, 7.54.

**5-exo-(Phenylsulfonyl)-5-endo-n-propylbicyclo[2.2.1]hept-2-ene (19b):** white prisms; mp 107–108 °C (from ethyl acetate/pentane);  $^1H$  NMR ( $CDCl_3$ , TMS)  $\delta$  7.83–7.18 (m, 5 H, Ph–), 6.23 (m, 1 H, olefinic H-2), 6.05 (m, 1 H, olefinic H-3), 3.43 (s, 1 H, bridgehead H-4), 2.88 (s, 1 H, bridgehead H-1), 2.59 (dd, 1 H,  $J = 9.8, 1.8$  Hz, H-6 exo), 2.34 (d, 1 H,  $J = 8$  Hz, H-7 anti), 1.60 (m, 1 H), 1.38 (d, 1 H,  $J = 8$  Hz, H-7 syn), 1.19 (m, 3 H) 0.90 (dm, 1 H,  $J = 10$  Hz, H-6 endo), 0.59 (t, 3 H,  $J = 6.2$  Hz, Me–);  $^{13}C$  NMR ( $CDCl_3$ ) 141.0, 139.7, 135.5, 133.5, 129.4, 129.3, 75.2, 48.4, 47.8, 43.0, 40.3, 37.3, 18.9, 14.8; IR (KBr) 3070, 2960, 1587, 1475, 1450, 1308, 1286, 1246, 1089; MS,  $m/z$  (%) 134 (22.7), 105 (36.3), 92 (22%), 91 (63.9), 79 (24.9), 78 (25.4), 77 (24.0), 66 (100), 65 (22.5), 64 (24.3). Anal. Calcd for  $C_{16}H_{20}O_2S$ : C, 69.53; H, 7.29. Found: C, 69.41; H, 7.44.

**Quenching of Anion 16 or 17 with  $D_2O$ .** After the usual workup the ratio of **20a:20b** (100:27) was determined by gas chromatographic analysis.

**2-(Phenylsulfonyl)[5,6- $^2H_2$ ]bicyclo[2.2.2]octane (21).** A stirred solution of 5-endo-(phenylsulfonyl)bicyclo[2.2.2]oct-2-ene (0.2 g, 0.806 mmol) in ethyl acetate (15 mL) was subjected to

catalytic deuteration (Pd on C 10%, 20 mg) at lecture bottle pressure and ambient temperature for 3 h. The mixture was filtered through Celite and the filtrate evaporated in vacuo. The solid residue was purified by recrystallization (ethyl acetate/petroleum ether) to give the pure sulfone (**21**) as white prisms: mp 58–59 °C; 0.193 g (0.77 mmol, 95%);  $^1H$  NMR ( $CDCl_3$ , TMS)  $\delta$  7.92–7.26 (m, 5 H, Ph–), 3.16 (m, 1 H H-2), 2.24 (d, 1 H,  $J = 12$  Hz, bridgehead H-1), 2.07 (m, 2 H), 1.72–1.35 (m, 6 H);  $^{13}C$  NMR ( $CDCl_3$ ) 139.1, 133.4, 129.1, 128.4, 62.4, 26.9, 26.7, 24.5, 24.4 (t,  $J = 19.4$  Hz), 24.3, 24.0, 20.8, (t,  $J = 19.7$  Hz); IR (KBr) 3032, 2950, 2872, 2188, 1452, 1305, 1280, 1238, 1154, 1092  $cm^{-1}$ ; MS,  $m/z$  (%) 143 (10), 111 (100), 77 (25), 69 (23), 68 (41), 67 (20). Anal. Calcd for  $C_{14}H_{16}D_2O_2S$ : C, 66.63; H(D), 7.19. Found: C, 66.95; H(D), 7.25.

**Quenching of Anion 22 with Chlorotrimethylsilane, Methyl Iodide, and Benzyl Bromide.** Method B was followed in each case with 1.1 equiv of butyllithium, sulfone **21**, and quenching with 3–5 equiv of the electrophiles. After the usual workup and purification by chromatography (silica, petroleum ether gradually increasing polarity to 7.5% ethyl acetate/petroleum ether), all spectroscopic data were consistent with the respective products. Detailed analysis of the  $^{13}C$  NMR revealed that each purified product was a mixture of endo and exo products. While it was impossible to accurately determine the epimeric ratio, crude estimations based on relative  $^{13}C$  NMR peak heights suggest that little or no stereoselectivity is observed in these reactions.

**Acknowledgment.** The award of a NATO collaborative grant to R.V.W. and P.C.B.P. is gratefully acknowledged.

**Supplementary Material Available:** Tables VI–IX of final atomic positions, bond angles, hydrogen atom parameters, and anisotropic thermal parameters for **1a** (4 pages). Ordering information is given on any current masthead page.

## Mechanistic Interpretation of Reactions with Opposing Signs of Field and Resonance Reaction Constants in the Dual Substituent Parameter Treatments of Taft, Yukawa–Tsuno, and Godfrey

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Fourteen reactions with opposing signs of field and resonance reaction constants  $\rho_F$  and  $\rho_R$  in Taft's dual substituent parameters (DSP) treatment are discussed mechanistically and compared, in part, with the corresponding evaluation by the DSP equations of Yukawa and Tsuno and of Godfrey. The experimental data are fitted best by Taft's treatment. Godfrey's claim that meta- and para-substituted benzene derivatives yield the same reaction constants  $\rho$  and  $\lambda$  cannot be verified for the dediazonation of arenediazonium ions. In addition to Taft's explanation for opposing signs of  $\rho_F$  and  $\rho_R$ , namely, positive charge moving closer to the substituent in going from reactant to transition state, it is shown here that a series of reactions (dediazonation, azide decomposition, addition reactions of aryl cations and of singlet carbenes) is characterized by concerted  $\sigma$  bond formation and back donation of  $\pi$  electrons between the two reagents.

Dual substituent parameter (DSP) relationships allow the separation of the influence of field (or inductive) and resonance effects of substituents on chemical reactivities and physical properties (e.g., electronic and NMR spectra, etc.) of organic compounds. In this paper we will discuss the rates of a series of reactions that show opposing influence of field and resonance effects and then use this series to compare three DSP relationships: those of Taft,<sup>1</sup>

of Yukawa and Tsuno,<sup>2</sup> and the recent proposal of Godfrey.<sup>3</sup>

(1) (a) Taft, R. W. *J. Am. Chem. Soc.* **1957**, *79*, 1045. (b) Ehrenson, S.; Brownlee, R. T. C.; Taft, R. W. *Prog. Phys. Org. Chem.* **1973**, *10*, 1.

(2) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 965, 971; **1966**, *39*, 2274.

(3) Fadhil, G. F.; Godfrey, M. *J. Chem. Soc., Perkin Trans. II* **1988**, 133. Godfrey, M. *J. Chem. Soc., Perkin Trans. II* **1988**, 138.

Taft's treatment<sup>1</sup> using eq 1 is widely applied.<sup>4</sup> It is an extension of the classical Hammett equation. Using appropriate substituent constants  $\sigma_F$  and  $\sigma_R$  for the field effect and for the resonance effect, one obtains the contributions  $\rho_F$  and  $\rho_R$  for the field and resonance influence, respectively, on the reaction rate constant  $k_X$  of X-substituted derivatives relative to that of the unsubstituted compound ( $k_0$ ). Among the hundreds of reactivities and

$$\log(k_X/k_0) = \rho_F\sigma_F + \rho_R\sigma_R \quad (1)^9$$

physical properties evaluated with eq 1, in all but a few cases the signs of both reaction constants  $\rho_F$  and  $\rho_R$  are the same, either both positive or both negative.

In 1973, only three reactions with opposing signs of  $\rho_F$  and  $\rho_R$  were known:<sup>1b</sup> the HCl-catalyzed formation of methyl esters of benzoic acids and the dediazonium of benzenediazonium ions and of benzoyl azides.<sup>10</sup> Taft and co-workers<sup>1b</sup> interpreted these cases of opposing signs by the statement that "... going from reactant to transition state, positive charge is moved closer to the substituent ( $\rho_F$  negative) ... and ... by a loss of reactant state *para* quinoidal resonance stabilization on achieving the transition state ( $\rho_R$  positive)".

The DSP equation of Yukawa and Tsuno<sup>2</sup> (2) is based on the substituent constants of two single substituent parameter equations, namely, the classical Hammett equation ( $\sigma$ ) and the Brown-Okamoto equation ( $\sigma^+$ ). The

$$\log(k_X/k_0) = \rho[\sigma_p = r(\sigma_p^+ - \sigma_p)] \quad (2)^{12}$$

value of  $r$  (greater or less than 1) implies conjugation of positive charge within the benzene ring that is larger or smaller than that for the definitive system. For  $r = 0$  the classical Hammett equation is obtained. There seems to be the general opinion in views of the Yukawa-Tsuno treatment that  $r$  is always positive (see Johnson,<sup>13a</sup> Exner<sup>14</sup>) but also doubts on the theoretical significance of  $r$  (Johnson,<sup>13b</sup> Jones<sup>15</sup>). We include the Yukawa-Tsuno equation in our investigation for the following reasons: (a) it has historical significance for the development of methods to differentiate substituent effects, (b) our expectation that negative  $r$  values may be present in the reactions of the type studied here, and (c) in order to compare its usefulness relative to the two other types of DSP treatment.

Fadhil and Godfrey<sup>3</sup> recently proposed eq 3, where  $\sigma_I$  is the inductive (field) substituent constant<sup>16</sup> and  $\sigma_{ST}$  (ST

$$\log(k_X/k_0) = \rho[\sigma_{ST} - \lambda(\sigma_{ST} - \sigma_I)] \quad (3)$$

(4) Analogous DSP treatments, but with smaller or larger differences with respect to the basis of the calculation of substituent parameters, were proposed by Charton<sup>5</sup> and by Swain and co-workers.<sup>6</sup> For a comparison of these DSP treatments and a triple substituent parameter treatment,<sup>7</sup> see Nakuzumi et al.<sup>8</sup>

(5) Charton, M. *Prog. Phys. Org. Chem.* 1981, 13, 119.

(6) Swain, C. G.; Lupton, E. C. *J. Am. Chem. Soc.* 1968, 90, 4328. Swain, C. G.; Unger, S. H.; Rosenquist, N. R.; Swain, M. S. *J. Am. Chem. Soc.* 1983, 105, 492.

(7) Taft, R. W. *Prog. Phys. Org. Chem.* 1983, 14, 247.

(8) Nakuzumi, H.; Kitao, T.; Zollinger, H. *J. Org. Chem.* 1987, 52, 2825.

(9) Until the mid-80's the field effect was called inductive effect, and therefore the respective parameters were labeled  $\rho_I$  and  $\sigma_I$ . Godfrey et al.<sup>3</sup> still use  $\sigma_I$ .

(10) In addition, two series of IR intensities were reported to have opposing signs for  $\rho_F$  and  $\rho_R$ .

(11) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* 1957, 79, 1913; 1958, 80, 4980.

(12) In order to differentiate the parameter  $r$  in eq 2 from regression coefficients in Table I, the former is denoted by italics.

(13) Johnson, C. D. *The Hammett Equation*; Cambridge University Press: Cambridge, 1973; (a) p 89; (b) p 90, 107.

(14) Exner, O. *Correlation Analysis in Organic Chemistry*; Plenum: New York, 1988; p 128.

(15) Jones, R. A. Y. *Physical and Mechanistic Organic Chemistry*; Cambridge University Press: Cambridge, 1984; p 44.

for standard) from a scale based on <sup>13</sup>C substituent chemical shifts of  $\beta$ -substituents in meta- and para-substituted styrenes. Equation 3 is formally analogous to the Yukawa-Tsuno equation (2). It is important, however, that the authors give different sets of  $\sigma_{ST}$  for meta and para substituents. As indicated by the subscripts in eq 2, the Yukawa-Tsuno equation is applicable to para derivatives only. For eq 1, Taft and co-workers investigated meta derivatives and concluded that the available data did not provide a sound basis for its application. DSP treatments of type 1 have, however, been applied several times to series of meta-substituted benzene derivatives, e.g., by Swain.<sup>6,17</sup> Godfrey claims the applicability of eq 3 to meta- and para-substituted compounds with different substituent constants but the same values of  $\rho$  and  $\lambda$  for the two positions.

The purpose of this paper is first to present other reactions with opposing signs of  $\rho_F$  and  $\rho_R$  in addition to those mentioned above, second to compare the results obtained with Taft's equation (1) with those of Yukawa and Tsuno (2) and of Godfrey (3), and third to discuss the mechanistic basis for the reactions with opposing field and resonance reaction constants  $\rho_F$  and  $\rho_R$  in addition to the explanation given by Taft and co-workers.<sup>1b</sup>

## Results

Since 1973, when Taft's compilation was published,<sup>1b</sup> only eleven additional reactions with opposing signs of  $\rho_F$  and  $\rho_R$  have been published.

Some proton transfer reactions show the phenomenon. They are called "double-labeled" reactions and have been evaluated by Taft and Topsom.<sup>18</sup> "Double-labeled" refers to the fact that a proton is transferred in these reactions from compounds labeled with a series of substituents in a specific position to the correspondingly substituted compounds of another series.

In addition to the dediazonium of aromatic diazonium ions in water, the same reaction has been studied since 1973 in less nucleophilic solvents<sup>8,19</sup> and with diazonium ion-crown ether complexes.<sup>8</sup> Among other types of reactions belong the addition of singlet carbenes  $\dot{C}XY$  to olefins forming cyclopropanes, studied by Moss and co-workers,<sup>20</sup> the  $N_\alpha N_\beta$  rearrangement of benzenediazonium ions,<sup>19</sup> and the addition of carbon monoxide to aryl cations (generated from benzenediazonium ions) in water, forming benzoic acids.<sup>21</sup>

The DSP results of all reactions with opposing signs of  $\rho_F$  and  $\rho_R$  are summarized in Table I. The table includes two reactions from which no opposing signs were found but which will be also discussed in this paper, namely, the decarboxylation of 2,6-dinitro-4-X-benzoic acids<sup>26</sup> and the reverse reaction of dediazonium.<sup>19</sup>

(16) Godfrey et al.<sup>3</sup> recommend using  $\sigma_I$  values from the following: Exner, O. In *Correlation Analysis in Chemistry: Recent Advances*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; Chapter 10.

(17) Swain, C. G.; Sheats, J. D.; Harbison, K. G. *J. Am. Chem. Soc.* 1975, 97, 783.

(18) Taft, R. W.; Topsom, R. D. *Prog. Phys. Org. Chem.* 1987, 16, 1.

(19) Ravenscroft, M. D.; Zollinger, H. *Helv. Chim. Acta* 1988, 71, 507.

(20) Moss, R. A. *Acc. Chem. Res.* 1980, 13, 58; 1989, 22, 15.

(21) Ravenscroft, M. D.; Skrabal, P.; Weiss, B.; Zollinger, H. *Helv. Chim. Acta* 1988, 71, 515.

(22) Hartman, R. J.; Borders, A. M. *J. Am. Chem. Soc.* 1937, 59, 2107.

(23) Taft, R. W. Personal communication, 1988.



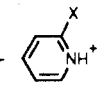
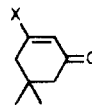
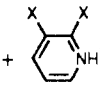

(24) Crossley, M. L.; Kienle, R. H.; Benbrook, C. H. *J. Am. Chem. Soc.* 1940, 62, 1400.

(25) Yukawa, Y.; Tsuno, Y. *J. Am. Chem. Soc.* 1957, 79, 5530.

(26) Segura, P. *J. Org. Chem.* 1958, 50, 1045.

(27) Moss, R. A.; Wlostowski, M.; Terpinski, J.; Kmiecik-Lawrynowicz, G.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* 1987, 109, 3811, and previous papers.

Table I. Reactions with Opposing Signs of Reaction Constants ( $\rho_F$  and  $\rho_R$ ) in the Taft Equation (1) and  $r$  Values in the Tsuno-Yukawa Equation (2)

no.	reactions <sup>a</sup>	reaction constants of eq 1 <sup>b,c</sup>			constants of eq 2		ref <sup>f</sup>	
		$\rho_F$	$\rho_R$	$n^d$	$r^{2e}$	$\rho$		$r$
1	esterification of ArCOOH with CH <sub>3</sub> OH, HCl-catalyzed	-0.527 (±0.05)	0.194 (±0.05)	6		-0.43 (±0.22)	-1.69 (±1.04)	22, 1b
2	proton transfer in ArC(CH <sub>3</sub> ) <sub>2</sub> + X- 	-2.8	9.3					18
3	proton transfer in ArCH <sub>2</sub> <sup>-</sup> + XC≡CH	18.0	-31.3					23
4	proton transfer in gas phase  + 	5.7	-12.4					18
5	proton transfer in gas phase  + 	1.7	-21.1					18
6	proton transfer in ArNH <sub>3</sub> <sup>+</sup> + X- 	-2.8	1.0					23
7	dediazonation of ArN <sub>2</sub> <sup>+</sup> in water	-4.09 (±0.20)	2.72 (±0.20)	5				24, 1b
8	dediazonation of ArN <sub>2</sub> <sup>+</sup> in 1,2-dichloroethane	-3.52 (±0.36)	2.26 (±0.42)	8	0.961	-3.18 (±0.97)	-3.08 (±6.3)	8
9	dediazonation of ArN <sub>2</sub> <sup>+</sup> in 2,2,2-trifluoroethanol (TFE)	-3.50 (±0.63)	2.21 (±0.23)	8	0.978	-3.39 (±1.15)	-4.01 (±1.58)	19
10	dediazonation of ArN <sub>2</sub> <sup>+</sup> /18-crown-6 ether complexes in 1,2-dichloroethane	-3.62 (±0.64)	2.75 (±0.74)	8	0.900	-3.03 (±1.81)	-1.82 (±0.58)	8
11	dediazonation of ArCON <sub>3</sub>	-0.14 (±0.01)	0.13 (±0.01)	5		-3.34 (±1.48)	-4.22 (±2.07)	25, 1b
12	N <sub>α</sub> N <sub>β</sub> rearrangement of ArN <sub>α</sub> ≡N <sub>β</sub>	-3.35 (±0.20)	2.47 (±0.07)	8	0.994	-0.13 (±0.06)	-3.29 (±1.07)	19
13	addition of CO to Ar <sup>+</sup>	2.77 (±0.83)	-0.59 (±0.36)	5	0.943	-3.31 (±1.49)	-1.90 (±0.44)	21
14	addition of olefins to singlet carbenes $\ddot{C}XY$	-0.53	1.10	10		1.87 (±0.95)	-2.01 (±1.10)	20 <sup>g</sup>
15	For comparison decarboxylation of 2,6-dinitro-4-X-benzoic acids	2.95 (±0.01)	1.62 (±0.01)	5	0.999	2.80 (±0.274)	-0.347 (±0.19)	26 <sup>h</sup>
16	reverse reaction of dediazonation of ArN <sub>2</sub> <sup>+</sup>	-0.18 (±0.09)	-0.32 (±0.06)	7	0.904	-0.12 (±0.08)	4.52 (±1.36)	19

<sup>a</sup>Ar indicates benzene derivatives with a series of substituents X in the para position. Reactions 1 and 6–14 are measured in solution, 2–5 are gas-phase reactions. <sup>b</sup>Reaction constants for reactions 1 and 6–14 are based on the scale of equilibrium constants (no. 6) and rate constants ( $k_X/k_0$ ); those of reactions 2–5 are based on the scale of  $\Delta G^\circ$  and a triple substituent parameter treatment (see Taft and Topson<sup>18</sup>). Their signs, but not their magnitude, are comparable with those of the other reactions. <sup>c</sup>Standard deviations in parentheses (if given in the original references). <sup>d</sup> $n$  = number of compounds. <sup>e</sup> $r^2$  = regression coefficient (if given in the original reference). <sup>f</sup>If two references are given, the first refers to the experimental data and the second to the DSP evaluation (Taft equation). Some of the references contain additional data on reaction constants with opposing signs for the same reaction systems. Those data are omitted because they do not give information that is relevant in the context of this paper. <sup>g</sup>Moss<sup>20,27</sup> evaluates his experimental results with selectivity values  $m_{CXY}$ . As selectivity is inversely related to reactivity we changed the signs of Moss'  $\rho$  constants for selectivity. <sup>h</sup>Calculation of  $\rho_F$  and  $\rho_R$  (using  $\sigma_{R(BA)}$ ) by the present author.

## Discussion

**DSP Reaction Constants.** The reason why Hammett's  $\sigma\rho$  relationship has been fairly well applicable for several thousand heterolytic reactions of substituted benzene derivatives since 1937 is by no means obvious. Depending on the location of the substituents in the electrophilic or in the nucleophilic partner of the respective reaction, positive or negative  $\rho$  constants, respectively, were obtained, having numerical values between about 15 and -15<sup>28</sup> if they were based on rate constants. In the Hammett equation  $\sigma$  and  $\rho$  comprise a combination of field and resonance effects. One can therefore conclude that in all these reactions both effects influence the reactivity in the same direction. Evaluating the same kinetic data with a DSP treatment, one expects therefore that  $\rho_F$  and  $\rho_R$  should have the same value. Experience shows that in the great majority of cases the ratio  $\rho_R/\rho_F = \lambda \cong 1$ . Values of  $\lambda$  larger than 1.1 or smaller than 0.9 (but still positive) are relatively rare: We estimate that they are present in fewer than 10% of all equilibria and rates for which a Hammett relationship was tested.

This result seems surprising as the field effect and the resonance effect are, in principle, independent of each other. One expects, therefore, reactions may be found in

which rates are enhanced by an electron-withdrawing field effect and an electron-donating resonance effect, or vice versa.

We will start the discussion of the reactions in Table I with the proton transfers in double-labeled systems (nos. 2–6). In reaction 2 a methyl proton of the aryldimethyl-carbenium ion is transferred to the pyridine nitrogen atom. It is clear that both this reaction and the protonation of para-substituted anilines by correspondingly  $\gamma$ -substituted pyridinium ions (no. 4) are excellent examples for Taft's explanation quoted in the Introduction. It is supported further by reaction 3, the transfer of an acetylenic proton to a benzyl carbonion, which, in a certain sense, is a "reverse" type of proton transfer to that of nos. 2 and 4. Indeed, the signs of  $\rho_F$  and  $\rho_R$  in no. 3 are both the opposite of those of nos. 2 and 4.

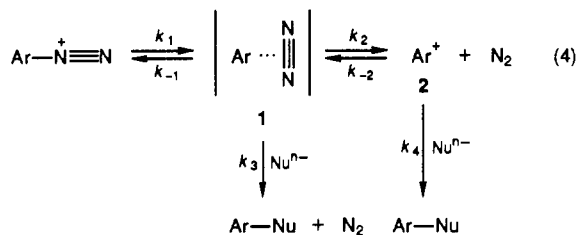
Reaction 3 is a case of negative charge migration. One should, however, not generalize Taft's charge migration rule in saying that, if *negative* charge is moved close to the substituent, opposing signs of  $\rho_F$  and  $\rho_R$  are to be found. This is shown by the decarboxylation of 2,6-dinitro-4-X-benzoic acid anions in water at 125 °C (no. 15). Negative charge moves closer to the aromatic ring and therefore closer to the substituent X in going from reactant to transition state. Accordingly,  $\rho_F$  is positive (not negative as for positive charge migration). Nevertheless, in this case the dominant  $\pi$ -donor reaction center is similarly moved closer and thus the value of  $\rho_R$  is also positive, i.e., a result

(28) For correlations of physical parameters, e.g., spectral data, etc., even more extreme positive and negative values of  $\rho$  were found.

that is a "classical" result like benzoic acid ionization.

Taft's charge migration rule can also be applied successfully to the other reactions of Table I (nos. 1 and 7-14). Additional conclusions and correlations can be drawn, however, from the opposing signs for reactions 7-14.

Consider the dediazonation of benzenediazonium ions in solvents of low nucleophilicity such as trifluoroethanol (TFE, no. 9). Kinetic results<sup>29</sup> are consistent with mechanism 4, involving the molecule-ion pair 1 as first intermediate, followed by the (solvated) cation 2. This mechanism is consistent with CNDO calculations.<sup>30</sup>



The secondary kinetic isotope effect found for 2,4,6-*d*<sub>3</sub>-benzenediazonium ion ( $k_{\text{H}}/k_{\text{D}_3} = 1.46$ )<sup>31</sup> is consistent with the structure shown in 1 for a molecule-ion pair with the NN triple bond perpendicular to the plane of the aryl cation, but not with a spirodiazirinephenonium ion structure, i.e., with covalent bonds between C<sub>1</sub> and the two nitrogen atoms. The rate constants for the same reaction in 1,2-dichloroethane (no. 8) are very similar. Solvent effects are small for aromatic dediazoniations.<sup>32</sup>

In water as a solvent, it can be shown<sup>33</sup> that the higher nucleophilicity of water decreases the activation barrier of direct formation of the molecule-ion pair 1 so much that the competitive reaction from 1 to product via 2 can no longer be detected. The reaction constants in water, however, are similar to those in TFE and in dichloroethane. This indicates strongly that the formation of the molecule-ion pair 1 is the dominant factor for the overall rate of dediazonation. This conclusion is supported by the rate constants of the N<sub>α</sub>N<sub>β</sub> rearrangement (no. 12). The numerical values of ρ<sub>F</sub> and ρ<sub>R</sub> for this rearrangement offer additional support for the equivalent character of the two nitrogen atoms in 1. The N<sub>α</sub>N<sub>β</sub> rearrangement also takes place in water, as found by Lewis et al.<sup>34</sup>

The substituent effects of the dediazonation of diazonium ion complexes with 18-crown-6 ether (no. 10) are surprisingly similar to those of diazonium ions solvated by the solvent only. This is, however, consistent with the small solvent effect of dediazonation. The dediazonation of azides (no. 11) is analogous to the reactions of benzenediazonium ions, as the β- and γ-nitrogen atoms of azides have the character of a diazonio group. The reaction constants are closer to zero because the N<sub>β</sub>N<sub>γ</sub> atoms are not a "full" diazonio group and because two (sp<sup>2</sup> hybridized) atoms are located between the substituted benzene ring and the (pseudo) diazonio group.

In reactions 7-12 the single bonds C<sub>1</sub>-N<sub>α</sub> (in no. 11 the N<sub>α</sub>N<sub>β</sub> bond) formally have to be broken. It is well-known, however, that the much higher stability of aromatic diazonium ions relative to aliphatic diazonium ions is due

to overlap of the aromatic π orbitals with the respective orbitals of the diazonio group. This overlap is influenced by substituents in the aromatic ring mainly by their resonance effect, whereas the strength of the s overlap of the (formal) single bond is a function of the field effect of other substituents (see below).

The reverse reaction of dediazonation, namely, the formation of benzenediazonium ions from aryl cations and molecular nitrogen (no. 15), cannot be studied directly as aryl cations can be generated in a simple way only by starting with benzenediazonium ions.<sup>35</sup> Substituted benzenediazonium ions labeled with <sup>15</sup>N in either the α or the β position were studied in the presence of a large excess of unlabeled molecular N<sub>2</sub>.<sup>19</sup> In this system the kinetics of replacing <sup>15</sup>N in the labeled diazonium ions by <sup>14</sup>N can be measured in TFE, in which the molecule-ion pair is not completely trapped by the solvent. It is, however, not possible under these conditions to obtain the intrinsic rate constants  $k_{-1}$  and  $k_{-2}$  in eq 4 from the overall rate constant of the isotope exchange. The measured rate constant is a complex mixture of all the intrinsic rate constants shown in eq 4. This mixture consists of two pairs of forward and reverse rates in equilibria ( $k_1/k_{-1}$  and  $k_2/k_{-2}$ ) and, at least, two product-forming steps. In conclusion, the substituent effects on the overall rates are expected to approximately cancel. This is indeed the case as the reaction constants are close to zero [ρ<sub>F</sub> = -0.18 (±0.09); ρ<sub>R</sub> = 0.32 ± 0.06].<sup>19</sup> A mechanistic evaluation of these ρ-values is impossible.

As discussed above the mechanism of dediazonation is simpler in water as the "detour" from the molecule-ion pair 1 via the aryl cation to products is no longer detectable. Mechanistic evaluation of the overall rate constant may, therefore, be easier. Unfortunately nitrogen molecules (besides the "internal" N<sub>2</sub> exchange of the molecule-ion pair 1) are not competitive enough with the good nucleophile H<sub>2</sub>O. Nevertheless, a better nucleophile than N<sub>2</sub> may be competitive with water. A suitable compound for this purpose is carbon monoxide, which is interesting in this context because it is isoelectronic with N<sub>2</sub>. Indeed, we obtained substituted benzoic acids in small yields as a product of dediazonation in water. The yields, which are a function of the substituent in the para position of the benzene ring, follow Taft's DSP equation fairly well (Table I, no. 13).

As expected for a reaction in which the bond formation of the molecule-ion pair with a nucleophile is rate-limiting, the signs of ρ<sub>F</sub> and ρ<sub>R</sub> are opposite of those of reactions 7-12, i.e., to dediazonation, to the N<sub>α</sub>N<sub>β</sub> rearrangement of benzenediazonium ions, and to the dediazonation of benzoyl azides, where C-N- (and N-N-) bond dissociation is the major factor of the reaction rate.

For comparison of the substitution of N<sub>2</sub> in 1 by CO to the respective substitution of N<sub>2</sub> in 1 by an "external" N<sub>2</sub> molecule, one has to consider that the highest occupied π orbital of CO is stabilized, as electrons are polarized toward oxygen. CO is, therefore, probably not added side-on like N<sub>2</sub>, but end-on. We will discuss this problem below in the context of orbital interactions.

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(33) Ravenscroft, M. D.; Takagi, K.; Weiss, B.; Zollinger, H. *Gazz. Chim. Ital.* 1987, 117, 353.

(34) Lewis, E. S.; Insole, J. M. *J. Am. Chem. Soc.* 1964, 86, 34. Lewis, E. S.; Hartung, L. D.; McKay, B. M. *Ibid.* 1969, 91, 419.

(35) See, however, the investigations of Speranza and co-workers<sup>36</sup> with tritiated benzenes and those of Sonoda et al.<sup>37</sup> with formation of phenyl cations containing two trimethylsilyl groups in ortho, ortho' position.

(36) Angelini, G.; Speranza, M.; Segre, A.; Altman, L. J. *J. Org. Chem.* 1980, 45, 3291. Angelini, G.; Fornarini, S.; Speranza, M. *J. Am. Chem. Soc.* 1982, 104, 4773.

(37) Himeshima, Y.; Kobayashi, H.; Sonoda, T. *J. Am. Chem. Soc.* 1985, 107, 5286.

(38) Rate constants  $k_3$  and  $k_4$  are even sums of at least two constants, namely, for reaction with TFE and with the counterion BF<sub>4</sub><sup>-</sup>, perhaps also with F<sup>-</sup>.

Moss and co-workers<sup>20,27</sup> investigated the reactivity of substituted singlet carbenes CXY with olefins by determining the reaction selectivity with mixtures of two olefins. They found that the selectivity index  $m_{CXY}$  follows a DSP correlation with opposite signs for the two  $\rho$  values ( $\rho_F = 0.53$ ;  $\rho_R = -1.00$ ). In qualitative terms, the Moss selectivity equation indicates that increasing  $\pi$  donation and increasing field withdrawal by substituents X and Y augment the selectivity of the singlet carbene CXY. Increasing selectivity corresponds to decreasing reactivity. We must, therefore, take the opposite signs of the two  $\rho$  values in the Moss selectivity relationship (Table I, no. 14).

The addition of olefins to carbenes has a negative  $\rho_F$  and a positive  $\rho_R$ , but the addition of CO to aryl cations has a positive  $\rho_F$  and a negative  $\rho_R$  value. In other words, the field and resonance effects of substituents in singlet carbenes reacting with double-bond systems are opposite to those of para substituents in aryl cations reacting with a multiple-bond system. We will discuss this result later in this paper.

**Comparison of Taft's DSP Reaction Constants with Yukawa and Tsuno's  $r$  Values and Godfrey's Reaction Constants  $\rho$  and  $\lambda$ .** In an earlier paper<sup>8</sup> we compared the application of the Taft DSP equation (1) in dediazonation with the corresponding DSP treatments of Charton<sup>5</sup> and Swain<sup>6</sup> as well as with Taft's more recent triple substituent parameter (TSP) model.<sup>7</sup> The result was that Taft's equation (1) gave the best fit for several sets of data. Charton's substituent constants fitted the data almost as well as Taft's.

It seems to be appropriate to make an analogous comparison with the Yukawa-Tsuno equation (2). Table I contains the  $\rho$  and  $r$  constants of eq 2 for those reactions for which experimental data are available in the literature. This is the first time that another DSP evaluation has been compared with the Yukawa-Tsuno treatment for the same experimental data.

Opposing field and resonance effects are reflected in eq 2 as negative values of  $r$ .<sup>39</sup> Standard deviations, however, are much larger than those of  $\rho_F$  and  $\rho_R$ . Regression coefficients are unacceptably low: the highest value of  $r^2$  is 0.785. The main reason for this low fit of eq 2 to data with opposing field and resonance effects is probably that ( $\sigma_p^+ - \sigma_p$ ) is a relatively small difference of two relatively large parameters and that both these substituent constants contain contributions from field and resonance effects. In spite of this statement we emphasize that Yukawa and Tsuno's work was a historically important (because it was early) and original contribution to the understanding of varying relative weights of field and resonance effects of substituents. No applications of Godfrey's equation (3) have yet been published. As Godfrey claims that it is also applicable to meta substituents we used eq 3 and Taft's equation (1) for dediazonation of meta- and para-substituted benzenediazonium ions. The experimental data are taken from Swain's work.<sup>17</sup> The results are given in Table II.

Standard deviations and regression coefficients indicate a slightly lower fit for the Godfrey treatment than for that of Taft. The reason may be analogous to the first argument that we gave (above) for the low fit of the Yukawa-Tsuno equation. A more grave result is the fact that both  $\rho$  and  $\lambda$  are different for the meta and for the para series,

**Table II. Comparative Evaluation of Dediazonation Rates of Meta and Para Substituted Benzenediazonium Ions in Water by Godfrey's and Taft's DSP Equations (2 and 1, Respectively)**

	reaction parameters		$r^2$	$n$
	$\rho$	$\lambda$		
eq 2 (Godfrey)				
para	-3.75 ( $\pm 0.57$ )	1.80 ( $\pm 0.21$ )	0.945	5
meta	-5.14 ( $\pm 0.42$ )	-0.39 ( $\pm 0.21$ )	0.968	6
eq 1 (Taft)				
para	-3.97 ( $\pm 0.30$ )	2.58 ( $\pm 0.19$ )	0.987	5
meta	-4.48 ( $\pm 0.24$ )	-1.79 ( $\pm 0.16$ )	0.991	6

in spite of Godfrey's claim that eq 3 yields the same values of  $\rho$  and of  $\lambda$  for meta and para substituents. That claim is not substantiated by evaluations of experimental data except for the basis set used for the substituent constants  $\sigma_{ST}$ . We will not, therefore, discuss the general applicability and the theoretical background of Godfrey's equation further in this paper.<sup>41</sup>

**Orbital Interactions in Reactions with Opposing Signs of  $\rho_F$  and  $\rho_R$ .** We will concentrate in this section on the dediazonation and the  $N_\alpha N_\beta$  rearrangement of aromatic diazonium ions, the addition of  $N_2$  and of CO to aryl cations, and the addition of singlet carbenes to olefins. A fairly large amount of semiempirical theoretical work on diazonium ions and aryl cations has been published since 1965.<sup>42</sup> Standard ab initio LCAO SCF molecular orbital calculations at the STO-3G level have been carried out since 1976.<sup>43-46</sup> With semiempirical and with ab initio methods the energy difference between the benzenediazonium ion and the transition state of the formation of the ion-molecule pair 1 in eq 4 is overestimated (356 kJ mol<sup>-1</sup> with MINDO/3,<sup>45</sup> 190 kJ mol<sup>-1</sup> in an ab initio study<sup>43</sup>) relative to the experimental activation energy ( $E_a = 114$  kJ mol<sup>-1</sup><sup>24</sup> in water, 117 kJ mol<sup>-1</sup> in TFE<sup>47</sup>). The calculated geometries, total charges, and  $\pi$ -electron populations of the benzenediazonium ion, the transition states, and the intermediates in reaction scheme 4 appear to be consistent with experimental data. Our conclusion<sup>31</sup> that a molecule-ion pair complex 1 is more likely for the intermediate than a spirodiazirinephenonium ion is supported by the calculations of Vincent and Radom<sup>43</sup> with respect to the (equal)  $CN_\alpha$  and  $CN_\beta$  distance in the intermediate (1.639 Å), but the calculated  $N_\alpha N_\beta$  bond length (1.216 Å) does not correspond well to expectations. Ab initio calculations with STO-3G standard geometry made by Dill, Schleyer, and Pople<sup>44b</sup> do not predict considerable substituent effects—in contrast to the experimental results.

(41) For a recent discussion of the controversies on the effects of  $\pi$ -electron demand on substituent resonance effects, see: Taft, R. W.; Abboud, J. L. M.; Anvia, F.; Berthelot, M.; Fujio, M.; Gal, J.-F.; Headley, A. D.; Henderson, W. G.; Koppel, I.; Qian, J. H.; Mishima, M.; Taagepera, M.; Ueji, S. *J. Am. Chem. Soc.* **1988**, *110*, 1797. They show that the simple product function  $R = \sigma_{PR}$  in a triple substituent parameter (including polarizability P) can describe resonance effects in gas-phase series well. We showed<sup>8</sup> that in dediazonations (in solution) polarizability is almost negligible.

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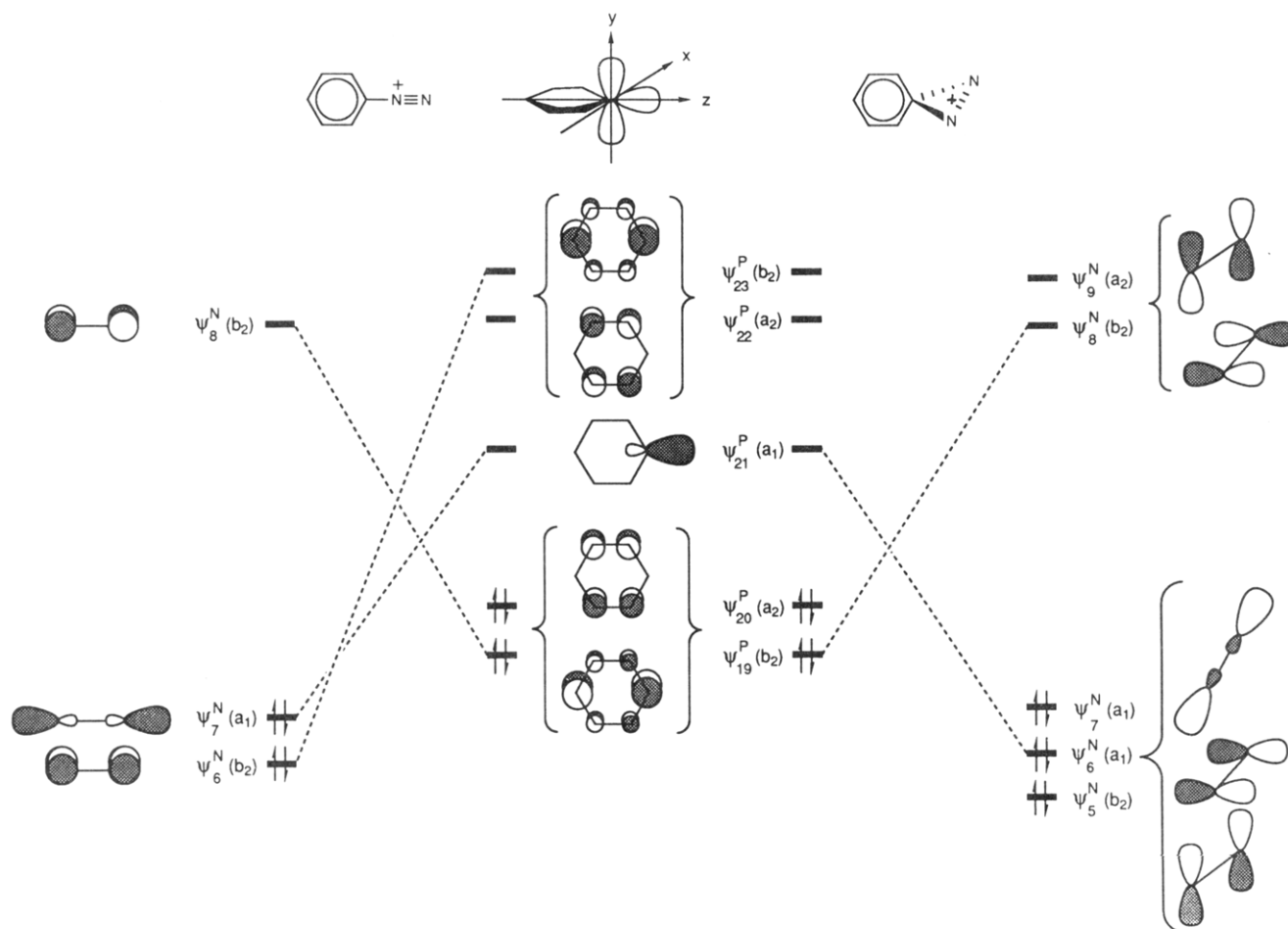
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(39) We found only one negative value for  $r$  in the literature:  $r = -0.1$  for the solvolysis of *cis*-2-arylcyclopentyl tosylates in HOAc.<sup>40</sup>

(40) Lancelot, C. J.; Cram, D. J.; Schleyer, P. v. R. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. 3, p 1392.



**Figure 1.** Important orbital interactions in the end-on and side-on addition of  $N_2$  to the phenyl cation (left-hand side and right-hand side, respectively). Orbitals classified under  $C_{2v}$  symmetry. Adapted from Vincent and Radom.<sup>43</sup>

More recently, however, Apeloig and Arad<sup>48</sup> calculated that silyl groups in the 2,6 positions should increase the stability of the phenyl cation. This result was subsequently confirmed by Sonoda's group.<sup>37</sup>

We will now discuss the relevant aspects of the opposing signs for the addition of  $N_2$  end-on and side-on to the aryl cation with the help of schematic orbital correlation diagrams (Figure 1). We use the same orbital classification as Vincent and Radom<sup>43</sup> ( $C_{2v}$  symmetry). For the approach of  $N_2$  in the  $xy$  plane of the aryl ring, i.e., side-on addition,  $\sigma$ -electron *withdrawal* by substituents will increase the  $a_1$ - $a_1$  interaction. A *positive*  $\rho_F$  constant is therefore expected for addition to para-substituted aryl cations.  $\pi$ -Electron donation by substituents will increase the  $b_2$ - $b_2$  interaction, for which a negative  $\rho_R$  constant is plausible. We cannot verify this conclusion by comparison with experimental data, as the addition of  $N_2$  to substituted aryl cations could only be followed qualitatively (see above). For the approach of  $N_2$  along the  $z$  axis, i.e. end-on addition, the  $a_1$ - $a_1$  interaction should be at least as strong as for the side-on reaction; a substantial positive  $\rho_F$  constant is therefore expected. The  $b_2$ - $b_2$  interactions should approximately cancel: Interaction of the two occupied orbitals should lead to a slight destabilization, but interaction with  $\pi^*$  should reduce the importance of the  $b_2$ - $b_2$  interaction relative to the  $a_1$ - $a_1$  interaction, i.e.  $|\rho_R| < |\rho_F|$ .

We cannot demonstrate this conclusion from the orbital interaction diagram experimentally for the addition of  $N_2$  to  $C_6H_5^+$ . The relationship  $|\rho_R| < |\rho_F|$  is, however, verified

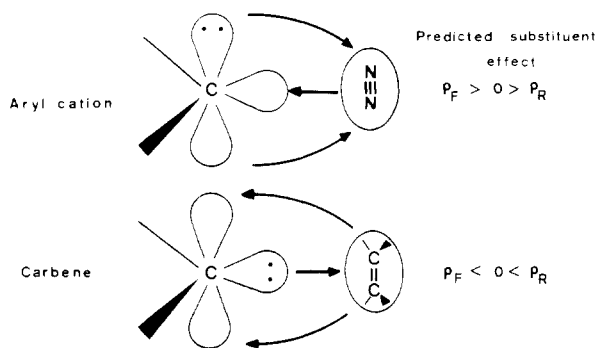
experimentally by the corresponding reaction with CO (Table I, no. 13).

On the basis of Figure 1 we can discuss qualitatively the effect of replacing  $N_2$  by CO for side-on and end-on addition to  $C_6H_5^+$ . For the approach of CO in the  $xy$  plane (side-on addition) it has to be considered that the  $\pi$  orbitals of CO are stabilized relative to those of  $N_2$ , as the electrons are polarized strongly toward oxygen. The  $\pi^*$  orbital is destabilized. The highly polar character of CO makes the side-on addition very unlikely. For the approach of CO along the  $z$  axis (C atom leading) the lone pair on C can interact more strongly than that of  $N_2$  with the unoccupied  $\sigma$  orbital of the phenyl cation than  $N_2$ . Substituents that are  $\sigma$  electron withdrawing will therefore increase the rate of reaction. A positive  $\rho_F$  constant, a negative  $\rho_R$  constant, and again the relationship  $|\rho_F| < |\rho_R|$  are expected. This is indeed the case (Table I, no. 13).

As mentioned previously, singlet carbenes are, to a certain degree, comparable with the phenyl cation. The difference, however, is that the HOMO orbital in  $C_6H_5^+$  is a  $p_y$  orbital, whereas in a singlet carbene it lies in the  $z$  axis (plane of  $\bar{C}XY$ ). In a singlet carbene, the LUMO is the  $p_y$  orbital. The orbital interactions in the reaction of a carbene with double- or triple-bond molecules such as olefins, CO, or  $N_2$  are therefore expected to be the reverse of the corresponding reactions with  $C_6H_5^+$ . This is indeed the case, as shown by the comparison of the DSP constants  $\rho_F$  and  $\rho_R$  for reactions 13 and 14 (Table I).

The two opposing HOMO-LUMO interactions for additions of aryl cations and carbenes to double-bond systems is shown schematically in Figure 2. For addition of aryl cations substituent effects are predicted corresponding to

(48) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1985**, *107*, 5285.



**Figure 2.** Orbital interaction scheme for reaction of aryl cations and singlet carbenes with multiple-bond systems.

DSP reaction constants  $\rho_F > 0 > \rho_R$ . For addition of singlet carbenes, however, the reverse sequence is expected:  $\rho_F < 0 < \rho_R$ .

For bond-breaking reactions (dissociations) opposite signs of  $\rho_F$  and  $\rho_R$  are found, as shown by dediazonation of arenediazonium ions (Table I, nos. 7 to 10) and of azides (no. 11), and by the  $N_\alpha N_\beta$  rearrangement of diazonium ions (no. 12) where  $C_1-N_\alpha$  bond cleavage is rate-limiting.

**Potential Candidates as Reactions with Opposing Signs of  $\rho_F$  and  $\rho_R$ .** Are there other reactions that might show analogous phenomena to the reactions in Table I? Interesting cases might be the thermal and photochemical dediazonation of diazoalkanes and related compounds (diazo ketones, etc.). No substituent effect studies suitable for a DSP evaluation seem to have been carried out under conditions where the product of dediazonation is a singlet carbene. Very little experimental work has been carried out on the reverse reaction of the diazomethane dediazonation. In 1964 Moore and Pimentel<sup>49</sup> showed in <sup>15</sup>N-labeling experiments that methylene, generated by the photolysis of either diazomethane or diazirine, reacts with  $N_2$  in a nitrogen matrix at 20 K to give diazomethane. Furthermore, photolysis of diazomethane or diazirine in <sup>15</sup>N<sub>2</sub> in the gas phase affords some conversion into labeled diazomethane.<sup>50</sup> In our own experience<sup>51</sup> the reactivity of carbenes in a solvent is, however, too low for reaction with  $N_2$ , either because the singlet  $\rightarrow$  triplet reaction is too fast or because of a very low intrinsic reactivity of the primarily formed singlet carbenes. Yamabe, Fukui, and co-workers<sup>52</sup> discussed the reactivity of singlet methylene with  $N_2$  from a theoretical point of view. They assumed that the electronic structure of a carbene as indicated in Figure 2 must first be transformed into the structure with an occupied  $p_y$ - and an unoccupied orbital in the HCH plane, i.e., into a less stable electron configuration.

Another group of addition reactions that may show substituent effects resulting in opposing  $\rho_F$  and  $\rho_R$  constants is the formation of  $N_2$ -metal complexes of transition metals. This possibility has been discussed by Yamabe et al.<sup>52</sup> and by us.<sup>53</sup> We are unaware of any investigations

on  $N_2$ -metal complexes that allow a test with DSP treatment.

An apparently similar reaction to the  $N_\alpha N_\beta$  rearrangement of diazonium ions (Table I, no. 12) is the isonitrile-nitrile rearrangement (5). As shown by R uchardt and



R = aliphatic, alicyclic, or aromatic residue

co-workers<sup>54</sup> in an extensive kinetic study of the rearrangement of 22 primary, secondary, tertiary, cyclic, bicyclic, bridgehead, benzyl, substituted benzyl,  $\alpha$ -carbo-methoxymethyl, triphenylmethyl, 9-triptycyl, and aromatic isonitriles, the rates are surprisingly uninfluenced by the structure and electronic properties of R. Aromatic isonitriles isomerize independently of polar para substituents and bulky ortho substituents. This rearrangement is obviously mechanistically very different from the  $N_\alpha N_\beta$  rearrangement of diazonium ions. As a consequence, R uchardt et al. did not propose a type of very weak bonding as in the molecule-ion pair 1 but a *hypervalent*  $sp^2$ -hybridized carbon  $C_1$  (of R) with relatively strong interactions to the orbitals of the NC group.

This comparison indicates that small changes of the orthogonal overlap have a large influence on the presence or absence of substituent effects. Common to both rearrangements is the possibility of excluding a phenonium ion type structure with an  $sp^3$ -hybridized  $C_1$  atom.

## Conclusions

It is surprising that there are relatively few organic addition and dissociation reactions known in which bond-making or bond-breaking, respectively, is realized by a field and a resonance effect of the opposing direction.

These reactions can be characterized most convincingly by a dual substituent parameter treatment such as that proposed by Taft. The separation of field effects from resonance effects is a classical problem of the influence of structural modifications on chemical reactivity. It has been discussed from a theoretical point of view by Streitwieser et al.,<sup>55</sup> Topsom<sup>56</sup> and others, and most recently by Niwa.<sup>57</sup> The relatively good correlation of experimental data with Taft's dual substituent parameters discussed in this paper allows convincing mechanistic explanations. This correlation demonstrates that empirical DSP treatments are well applicable even to cases in which field and resonance effects have opposing influence.

Nevertheless, the main question is still open: What is the basic reason that there are thousands of reaction rates and equilibria for which the classical Hammett equation and slight modifications (e.g. Brown's  $\sigma^+$  scale) can be used—a fact which means that the field and the resonance effects operate in the same direction—but that there are only few processes in which the field and resonance effect have opposing directions.

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