

REGARDING PROTONATED CARBONYL DERIVATIVES AND
THEIR CONJUGATIVE ACCEPTOR CAPACITIES

I. R. Fox, P. L. Levins and R. W. Taft, Jr.

College of Chemistry and Physics, The Pennsylvania
State University, University Park, Pa.

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WE report herein results which are pertinent to three matters of current interest: the relative conjugative charge-accepting capacities of protonated and unprotonated carbonyl compounds,¹ the question of the preferred site of protonation of amides,^{1,2} and the correlation of NMR and reactivity parameters.³

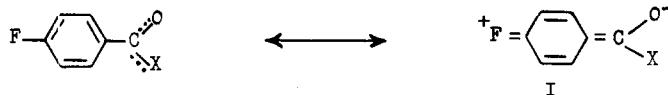
Currently the most discriminative measure available of the order of conjugative charge release and withdrawal by substituent groups in ground state molecules is the fluorine atom mesomeric charge perturbation (m.c.p.) due to m- and p-substituents in fluorobenzenes.³ As previously defined:⁴ m.c.p. = $-(\delta_{\text{p}}^{\text{F}} - \delta_{\text{m}}^{\text{F}})$, where $\delta_{\text{m}}^{\text{F}}$ refers to the F^{19} NMR shielding parameter of a meta-substituted fluorobenzene and $\delta_{\text{p}}^{\text{F}}$ refers to that for the corresponding para isomer.

For uncharged $+R$ substituents enhanced positive m.c.p. values have been

¹(a) R. Stewart and K. Yates, J. Amer. Chem. Soc. 80, 6355 (1958); 82, 4059 (1960)
(b) K. Yates and R. Stewart, Canad. J. Chem. 37, 664 (1959);
(c) J.T. Edward, H.S. Chang, K. Yates and R. Stewart, Ibid. 38, 1518 (1960)

² G. Fraenkel and C. Franconi, J. Amer. Chem. Soc. 82, 4478 (1960) and references given therein.

attributed to the interaction represented by:^{3,4}



Since the interaction structure (I) involves a relatively long-range charge separation, it is of interest to have information concerning the relative importance of such an interaction structure and the analogous interaction structure (II), which involves charge re-distribution; e.g.



We have measured m.c.p. values directly in very dilute 99.8% H_2SO_4 solutions containing m-substituted fluorobenzene and its p-isomer, the substituent in each case corresponding to the general formula COX (X's are as listed in Table I). Under these conditions, it is known that for all practical purposes each of the substituent groups is completely protonated.¹ Comparison of the m.c.p. values for corresponding protonated and unprotonated substituents (items 1 and 2 of Table I) indicates that charge withdrawal from fluorine is on the order of 3-fold greater for the former. Thus the expectation⁵ that form (II) tends to make a substantially greater contribution to its resonance hybrid than does form (I) is confirmed. It is noteworthy, however, that the group X has a strong modulating influence on the acceptor capacity. Thus, the largest m.c.p. (greater downfield shift and electron withdrawal from F) for the uncharged COX substituents (COF) is only somewhat smaller than the smallest m.c.p. for a protonated substituent

³ For recent review and earlier references, cf. R.W. Taft, Jr., J. Phys. Chem. 64, 1805 (1960).

⁴ R.W. Taft, Jr. et al., J. Amer. Chem. Soc. 82, 756 (1960); cf. also H.S. Gutowsky et al., Ibid. 74, 4809 (1952).

⁵ cf., for example, R.S. Mulliken, Tetrahedron 5, 256 (1959).

TABLE I. CORRELATION OF PROPERTIES OF ARCOX COMPOUNDS^a

X	σ_R^0	σ_I	(1) M.c.p. (in p,p-m.) F-Ar-C(OH)X ⁺	(2) M.c.p. (in p,p-m.) F-Ar-COX, 99.8% H ₂ SO ₄	(3) ArX resonance effect, ³ Ioniz. CH ₃ O-C(OH)X ⁺ log(K/K ₀) - σ^0 (calc.)	(4) pK _a C ₆ H ₅ C(OH)X ⁺	(5) pK _a Values C ₆ H ₅ C(OH)X ⁺	(6) U.V.Absorp- tion Max. C ₆ H ₅ C(OH)X ⁺ , ^{mp} obs. calc.	(6) U.V.Absorp- tion Max. C ₆ H ₅ C(OH)X ⁺ , ^{mp} obs. calc.
			obs. ^b	calc.	obs. ^b	calc.	obs. ^b	calc.	obs. ^b
O ⁻	-0.60 ^j	-0.12 ^j	6.6 ^c	6.2	3.1 ^d	2.7	-0.1	+ 4.4	235 ^e
NH ₂	- .48	+ .10	13.2	13.8	4.6	5.3	- .2	- 2.2	234 ^g
OH	- .40	+ .25	19.5	18.8	6.6	7.0	- .5	- .6	225 ^h
OC ₂ H ₅	- .41	+ .25	18.0	18.4	6.7	7.0	- -	- .6	225 ^g
CH ₃	- .10	- .05	27.5	28.4	7.3	7.5	-1.1	-1.1	262 ⁱ
H	.00	.00	33.9	33.2	9.0	8.7	-1.4	-1.3	260 ⁱ
F	- .34	+ .52	-	24.3	10.1	9.5	- -	- .9	287 ^j
							-13.8	- -	298 ^j
								270 ^j	251 ^j
								-	253 ^j
								-	238 ^j
Equation: Correlation Coeff., R			$m.c.p.^t = 42.8\sigma^0_R + 10.85\sigma_I + 33.2$	$m.c.p.^0 = 8.5\sigma^0_R + 7.36\sigma_I + 8.7$	$\log(K/K_0) - \sigma^0 = \log(K/K_0) - \sigma^0 =$ $-1.876\sigma_R - 0.445\sigma_I - 1.3$	$pK_a^t = -16.6\sigma^0_R - 22.5\sigma_I - 8.0$	$\lambda^+ = 10.4\sigma^0_R + 17.6\sigma_I + 298$	$\lambda^0 = 10.4\sigma^0_R + 17.6\sigma_I + 298$	
			0.994	0.944	0.985	0.947	0.989	0.972	

a. Items 3-6 are based upon data given in ref. 1.

b. M.c.p. values were obtained⁴ in 99.8% H₂SO₄ solutions containing equimolar quantities of the m- and p-isomers at 10%, 7.5%, and 5% by volume of each and the results extrapolated linearly to 0%.c. Data for the CO₂H group in 75% aq. CH₃OH.d. Obtained in dilute 75% aq. CH₃OH containing excess base.e. Obtained in 56-63% H₂SO₄.f. Obtained in 95.99.5% H₂SO₄.

g. Obtained in 0.01 M NaOH.

h. Obtained in H₂Oi. Obtained in 4.4% H₂SO₄.j. Obtained from ¹⁹F NMR shielding parameters for m- and p-fluorophenols in dilute 7% aq. CH₃OH containing excess base; cf. ref. 3.

$(COHNH_2^+)$; and, in general, among the m.c.p. values of Table I a nearly continuous gradient is apparent.

Recent NMR evidence indicates that O-protonation is substantially favored over N-protonation in aliphatic amides.² However, Stewart *et al.* have presented an argument favoring N-protonation of benzamide as the result of valuable basicity studies of substituted benzoyl derivatives.^{1*} Their argument is based upon the observation that the pK_a 's of protonated p-substituted acetophenones, benzaldehydes and benzoic acids are better correlated by σ^+ than σ values, whereas the converse holds for protonated benzamides. The present results indicate that the observations of Stewart *et al.* are very likely not due to predominant N-protonation of the benzamides but rather result from the attenuating of conjugation between a -R para-substituent and the $C(OH)X^+$ group, produced by increasing conjugative charge-release from the group X.

We reach this conclusion through the fact that six chemical and physical properties (cf. Table I) are correlated to reasonable approximation (more precise correlations are not expected for several apparent reasons) for these systems by the equation:⁶ $P = \sigma_I \rho_I + \sigma_R^0 \rho_R$, where σ_I and σ_R^0 are substituent parameters³ referring to the group X and ρ 's are susceptibility parameters. These correlations demonstrate in a roughly quantitative way that increasing conjugative charge-release (corresponding to increasing negative values of σ_R^0) from X decreases the effects resulting from resonance interaction between the carbonyl derivatives and the benzene (or substituted benzene) ring in a regular manner. If predominant O-protonation were not involved with the benzamides as well, these regularities would not be expected to hold.

⁶ R.W. Taft, Jr., *J.Amer.Chem.Soc.* 79, 1045 (1957); *Ibid.* 79, 5075 (1957). The wide variation of the ratio of the inductive and resonance blending coefficients, ρ_I and ρ_R , precludes adequate correlation of the data of Table I by any single substituent parameter equation.

*Note Added in Proof: cf., however, R. Stewart and L.J. Muenster, *Canad. J.Chem.* 39, 401 (1961).