mm.[22] which was obtained by the static method and is expected to be somewhat lower than our value because of association in the methanol vapor. From these and other observations, we conclude that our apparatus yields precise vapor densities at flow rates less than *ca.* 9 l./hr., and that at higher flow rates the difficulty appears to be incomplete vapor condensation rather than incomplete vapor saturation.

The values of p_0 and H obtained in this study are recorded in Table I, along with their average deviations. Each p_0 value represents the average of at least four measurements and each H value the average of at least eleven measurements involving at least two different batches of solvent and at least four different solutions.

Kinetic Measurements.—For a kinetic run, a weighed amount of the benzyl chloride was mixed with a weighed amount of methanol which was contained in a glass-stoppered flask and which had reached temperature equilibrium with the constant temperature bath at 25.05 ± 0.01°. At appropriate time intervals, the appropriate weight of solution was pipetted into five times its volume of acetone and 2 ml. of a 0.1% solution of lacmoid in ethanol was added. The solution was then titrated to the lacmoid end-point with *ca.* 0.005 *N* base which had been standardized against sulfamic acid in the same medium and with the same indicator. The solvent titer was found to be negligible. Six to twelve aliquots were taken in each kinetic run, extending over the range 0–5% reaction with benzyl chloride and 0–25% reaction with the *p*-alkylbenzyl chlorides.

Rate constants were calculated from the equation, $\log[1/(a - x)] = (k_s/2.303)t - C$, where a is the initial concentration of the benzyl chloride as calculated from the weights of reactant and solvent, x is the concentration of acid as determined by titration, t is the time, C is the (undetermined) constant of integration and k_s is the specific first-order rate constant. The rate constant was taken as the slope, multiplied by 2.303, of the best visual straight line drawn through the points in a plot of $\log[1/(a - x)]$ *vs.* t.

The rate constants obtained are recorded in Table I along with their average deviations. Each value is the average from at least four different kinetic runs, half of which were made before, and half after, the vapor pressure measurements, and which involved at least two different batches of solvent. The kinetic solutions were all *ca.* 0.01 molal in the benzyl chlorides except with benzyl chloride itself, for which kinetic runs were made with *ca.* 0.1 molal solutions as well, and for which the rate constant was found to be independent of concentration. For each benzyl chloride, two kinetic runs were made in solvent to which sufficient water had been added to make it *ca.* 0.1% by wt. water (10 times the water concn. in the pure solvent). In each case, the specific rate constant was identical with that obtained in the pure solvent.

Calculations.—For each benzyl chloride, the free energy of solvation corresponding to the transfer of 1 mole of pure substance to the hypothetical 1 molal solution was calculated from the equation, $\Delta F_{\text{solv}} = 2.303\ RT \log H/p_0$. The ratio of "intrinsic" specific rate constants, k'_g/k_g, was taken as lying between the limits defined by the expressions, $(k'_s/k_s)\cdot e^{-(\Delta F'_{\text{solv}} - \Delta F_{\text{solv}})/RT}$ and $(k'_s/k_s)e^{+(\Delta F'_{\text{solv}} - \Delta F_{\text{solv}})/RT}$ which simplify to $(k'_s/k_s)(Hp'_0/H'p_0)$ and $(k'_s/k_s)(H'p_0/Hp'_0)$. The values obtained are recorded in Table I.

Acknowledgment.—We are greatly indebted to the National Science Foundation for its support of this work through NSF grant number G-5116.

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[22] D. E. Dever, A. Finch and E. Grunwald, *J. Phys. Chem.*, **59**, 668 (1955).

[CONTRIBUTION FROM THE DOW CHEMICAL CO., EASTERN RESEARCH LABORATORY]

Electronic Interactions in Phenyl Acetates and Acetanilides[1]

BY H. H. FREEDMAN

RECEIVED AUGUST 24, 1959

The relative importance of an inductive *vs.* a resonance mechanism for the high carbonyl absorption frequency of phenyl acetate and acetanilide has been investigated. A study of the C=O frequency shifts in their *m*- and *p*-substituted derivatives clearly shows that the inductive mechanism is responsible for the frequency shift in phenyl acetate, but a resonance mechanism is more appropriate in the acetanilides. This is supported by a study of their respective Stuart–Briegleb molecular models which, on the basis of steric inhibition of resonance due to lack of coplanarity within the molecule, indicates that a resonance mechanism is relatively unimportant in phenyl acetate.

It has been long known that the introduction of an unsaturated group on the alcohol moiety of an ester, as in phenyl or vinyl acetate, causes a shift to higher frequency in the ester carbonyl stretching band.[2,3] Thus Hartwell[4] found that methyl, vinyl and phenyl acetate absorb at 1747, 1762 and 1766 cm.$^{-1}$ in the liquid state and Jones[5] reported a carbonyl frequency increase of 30 cm.$^{-1}$ in steroid acetate esters when cycloalkyl is replaced by phenyl. A similar though lesser displacement is observed with amides, and this was first reported by Richards and Thompson[6] who noted that the carbonyl band of acetanilide was at a distinctly higher frequency than that of N-alkyl substituted amides.

Two explanations have been offered for these carbonyl shifts. The simpler of these maintains that the high frequency of vinyl acetate is due to the replacement of the electropositive alkyl group by the electronegative vinyl, the latter "increasing the electron-attracting power of the oxygen atom in the —O—CH=CH$_2$ group, thus diminishing the ionic character of the carbonyl link."[4] Rasmussen and Brattain[7] support this hypothesis and point out that 1,1-diacetoxypropane, $CH_3CH_2CH(OCOCH_3)_2$, also exhibits its ester band at shorter wave lengths than normal (1761 cm.$^{-1}$) and that this must be due to the mutual effect of the negative acetoxy groups. Presumably, then, this effect is directly analogous to that of α-halogenated ketones whose enhanced C=O frequencies have been directly attributed to the inductive (and field) effect of the electronegative halogen.[8] For

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[1] Presented in part at the Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June, 1958.

[2] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 182.

[3] R. N. Jones and C. Sandorfy in "Chemical Applications of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, Chap. IV, p. 483.

[4] J. H. Hartwell, R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1436 (1948).

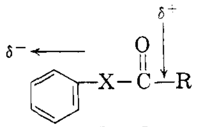
[5] R. N. Jones, *et al.*, THIS JOURNAL, **74**, 2820 (1952).

[6] R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, 1248 (1947).

[7] R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

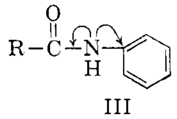
[8] Reference 3, p. 474.

the case of phenyl acetate (I) and acetanilide (II) we may then imagine the inductive effect of the phenyl group being transmitted to the carbonyl *via* the oxygen and nitrogen atoms, respectively.

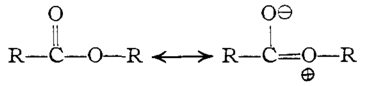


I, X = O
II, X = NH

An alternative explanation for the band shifts has been given in terms of the familiar resonance theory. Thus, in the case of acetanilide, Richards and Thompson[6] suggest that the electron-attracting phenyl "can be regarded as opposing the conjugation from the nitrogen atom to the carbonyl group," as in III, while a completely equivalent explanation has been offered by Jones[9] for phenyl acetate: namely, that the usual ester resonance (IV) is suppressed by competition of the system (V) for the electrons of the ester oxygen atom. Finally, Bellamy[10] states that in vinyl acetate there is an internal cancellation of mesomeric effects and attributes the abnormally short wave length to the lack of contributions from resonance forms such as IV.

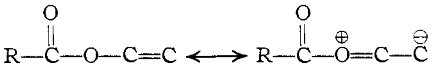


III



$$\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}R} \longleftrightarrow \mathrm{R{-}\overset{\displaystyle O^{\ominus}}{\overset{|}{C}}{=}\underset{\oplus}{O}{-}R}$$

IV



$$\mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}C{=}C} \longleftrightarrow \mathrm{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\oplus}{O}{=}C{-}\overset{\ominus}{C}}$$

V

It is well known that the carbonyl group is very sensitive to both resonance and inductive effects. These may act to either increase or decrease the carbonyl frequency and may even act in opposition, thus making it extremely difficult to separate the two, or even predict which effect will predominate in a given case. This certainly applies to the present situation and from the evidence available in the literature to date, it would be very difficult to choose between an inductive or resonance mechanism or a combination of both. Further, the possibility exists that the C=O frequency shifts may be caused by different mechanisms in the anilides and phenyl acetates. This last alternative appears to be the correct one; from a study of both the molecular structure of phenyl acetate and acetanilide, as well as the carbonyl frequency shifts of their nuclear-substituted derivatives, we have concluded that an inductive mechanism explains the shifts in the phenyl acetates while a resonance mechanism is primarily responsible for the shifts in the acetanilides.

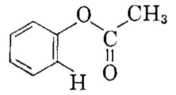
Experimental

The spectra were obtained on a Baird model 4–55 double beam spectrophotometer equipped with sodium chloride optics. Calibration and paper alignment difficulties were minimized by recording the 6.238 μ polystyrene band on each spectrum. The compounds were examined as dilute solutions (1×10^{-2} *M* maximum) in 0.1- or 1.0-mm. matched cells, depending upon solubility and the intensity of the carbonyl band. The maximum error in the 6 μ region is estimated to be 0.01 μ and in most cases, where the sharpness of the carbonyl band was maintained by the use of sufficiently dilute solutions, the wave length could be read and reproduced to 0.005 μ (± 1.5 cm.$^{-1}$). Where possible, the compounds were examined in carbon tetrachloride solutions. However, the limited solubility in this solvent necessitated in some cases the use of chloroform or dioxane.

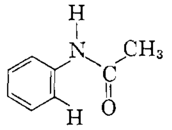
All but one of the acetophenones were commercially available compounds of a good grade of purity. *m*-Methoxyacetophenone was prepared by alkylation of *m*-hydroxyacetophenone (Aldrich Chemical Co.) with dimethyl sulfate. The majority of the acetanilides and phenyl acetates were prepared from the corresponding commercially available aniline or phenol by the usual technique of acetylation with acetic anhydride in the presence of sodium acetate. An exception to this is *p*-aminophenyl acetate, which was prepared from benzilidene-*p*-aminophenol by the method of Galatis.[11] The purity of the acetylated products was ascertained both by comparing their physical constants with those reported in the literature and noting the absence of amine or phenolic starting material in the 3μ region of its spectrum.

Discussion

Structure Studies.—Since one of the primary requirements for resonance interaction between two groups is that they be mutually coplanar, it is fundamental to any discussions of electronic interactions in phenyl acetate and acetanilide to examine their molecular structure. Accordingly, an approximate evaluation of the relative steric effects was obtained by examining their Stuart–Briegleb models. The assumption that phenyl acetate (VI) exists with the phenyl and carbonyl groups having a *cis* relationship is in agreement with previous infrared results,[12] dipole moment measurements[13] and electron diffraction studies[14] of simple aliphatic esters. Similarly, an X-ray diffraction study of the crystal structure of acetanilide[15] has shown that the phenyl and carbonyl groups have a *cis* relationship as in VII and this has been verified for other N-substituted amides by a study of their electric moments.[16] The fact that this *cis* structure is not merely characteristic of the crystalline state but actually persists in dilute solutions can be inferred from the work of Russell and Thompson[17] who showed that the presence of *trans* isomer can be detected by the presence of a second NH stretching band in the 3μ region; since



VI



VII

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[9] Reference 3, p. 482.

[10] L. J. Bellamy, *J. Chem. Soc.*, 4221 (1955).

[11] L. Galatis, *Ber.*, **59**, 848 (1926).

[12] J. K. Wilmhurst, *J. Molecular Spectroscopy*, **1**, 201 (1957).

[13] R. Marsden and L. E. Sutton, *J. Chem. Soc.*, 3183 (1936).

[14] J. M. O'Gorman, W. Shand, Jr., and V. Schomaker, THIS JOURNAL, **72**, 4222 (1950).

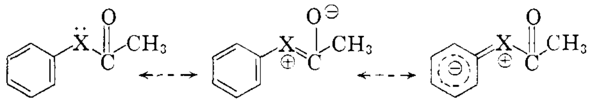
[15] C. C. Brown and D. E. C. Corbridge, *Acta Cryst.*, **7**, 711 (1954).

[16] J. E. Worsham, Jr., and M. E. Hobbs, THIS JOURNAL, **76**, 206 (1954).

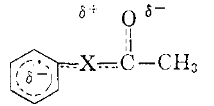
[17] R. A. Russell and H. W. Thompson, *Spectrochim. Acta*, **8**, 138 (1956).

only one band is present in the spectrum of acetanilide in any of the common infrared solvents, we may assume that it exists entirely in the *cis* form. However, diffraction studies have shown that there is a fundamental difference between the ester and amide groups. Whereas acetamide and N-methylacetamide are planar or nearly so,[18,19] methyl acetate has an average angle of 25° between the acetyl and methoxyl planes.[13] This difference is greatly magnified in the O- and N-phenyl substituted compounds, and is discussed in detail below.

Resonance interactions in phenyl acetate (VIII–X, X = O) and acetanilide (X = NH) may be evaluated by considering the steric requirements for the hybrids IX and X, and how well these requirements are met by the actual molecules. Modern theory predicts that in the dipolar ion IX resonance will be at a maximum when the phenyl carbon attached to the X atom and the methyl group are coplanar and will be minimized when rotation about the carbonyl–X bond brings them 90° out of plane. Similarly, for the dipolar form X, complete resonance interaction requires coplanarity of the phenyl ring and the X to carbonyl–carbon bond. However, if both hybrids IX and X contribute appreciably to the actual structure as in XI, then the steric conditions for this cross-conjugated system become much more stringent inasmuch as the entire molecule must now be uni-planar. If the reasonable assumption is made that neither IX nor X is present to the total exclusion of the other, then we must accept XI (or a combination of IX and X) as representing the actual state of the resting molecule. This means that deviation from planarity of the molecule as a whole will be effected not by maintaining planarity about the X–carbonyl bond at the expense of the phenyl–X bond or *vice versa*, but by a compromise between these two extremes. Therefore, if these extreme angles can be estimated, then the deviation from coplanarity of the molecule should be, to a first approximation, equal to their mean value.



VIII IX X



XI

An estimation of the value of these extreme angles may be obtained from a visual inspection of the Stuart–Briegleb molecular models of acetanilide and phenyl acetate. In constructing the former molecule the use of an sp^2-hybridized nitrogen atom with bond angles of 120° rather than an sp^3-nitrogen is in keeping with the modern view of the amide group and is specifically indicated by the ultraviolet work of Wepster[20] on substituted acetanilides. In the absence of other data, the usual ether-type of oxygen atom was used for phenyl acetate. In the discussion which follows, we shall refer to θ_1 as the angle formed by rotation about the hetero atom–carbonyl bond, and θ_2 as the angle formed by the rotation about the hetero atom–phenyl bond. In effect then, θ_1 refers to the extent of planarity within the amide or ester portion, respectively, and when equal to zero implies that a 100% contribution from structures such as IX is theoretically possible. Similarly, θ_2 is concerned with the aniline or phenol planes, respectively, the deviations from planarity of this portion of the molecule determining the contributions from structures such as X.

For acetanilide it is found that steric repulsion between the carbonyl and the *ortho*-H almost certainly exists when the entire molecule is uniplanar. When this steric interference is eliminated by first maintaining $\theta_1 = 0$ and observing θ_2 and then performing the converse operations, we obtain values of $\theta_1 = 30°$ and $\theta_2 = 45°$. The mean value of 37.5° for the average angle formed by the aniline and acetyl planes compares very favorably, considering the inadequacies of this procedure, with the reported value of 38° obtained from an X-ray diffraction study.[15]

The deviations from planarity of the much more sterically-crowded phenyl acetate molecule has not been reported, but by applying the above procedure we find that $\theta_1 = 55°$ and $\theta_2 = 65°$. The mean value for the angle formed between the phenol and the acetyl planes is now 60°, or almost twice that of acetanilide.[21] Now if we use the approximate relation, $E_R = (\cos^2\theta)$[23,24] to calculate the percentage of the total available resonance energy retained by these structures, we find that this is approximately 65% for acetanilide and only 25% for phenyl acetate. In effect, then, a resonance mechanism for the increased carbonyl force constant of these compounds is almost three times as important in acetanilide as in phenyl acetate and this conclusion is supported by our infrared studies of their nuclear-substituted derivatives.

Infrared Studies.—It has been well established that the aromatic carbonyl band shifts offer a sensitive method for the detection of the electronic interactions of a substituent with the aromatic ring.[25] In the absence of any complicating steric, bonding or solvent interactions, these shifts may be directly attributed to the change of electron density at the carbonyl group caused by a combination of resonance and inductive effects engendered by the substituent.[26,27] Insofar as the Hammett σ-constants are also measures of the electron

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[18] F. Senti and D. Harker, This Journal, **62**, 1008 (1940).

[19] G. Albrecht and R. B. Corey, *ibid.*, **61**, 1087 (1939).

[20] B. M. Wepster in "Progress in Stereochemistry," Vol. 2, Academic Press, Inc., New York, N. Y., 1958, pp. 148–150.

[21] It has been observed[22] previously that it is impossible to construct a model in which the C=O group is coplanar with the phenyl group and that therefore there is no conjugation between the C=O and the phenoxy group.

[22] D. Cook, This Journal, **80**, 49 (1958).

[23] E. A. Braude in "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, Chap. 4, pp. 173–174.

[24] E. A. Braude in "Progress in Stereochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1954, p. 142.

[25] Reference 2, p. 138.

[26] R. N. Jones, W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 504 (1957).

[27] Reference 3, p. 473 ff.

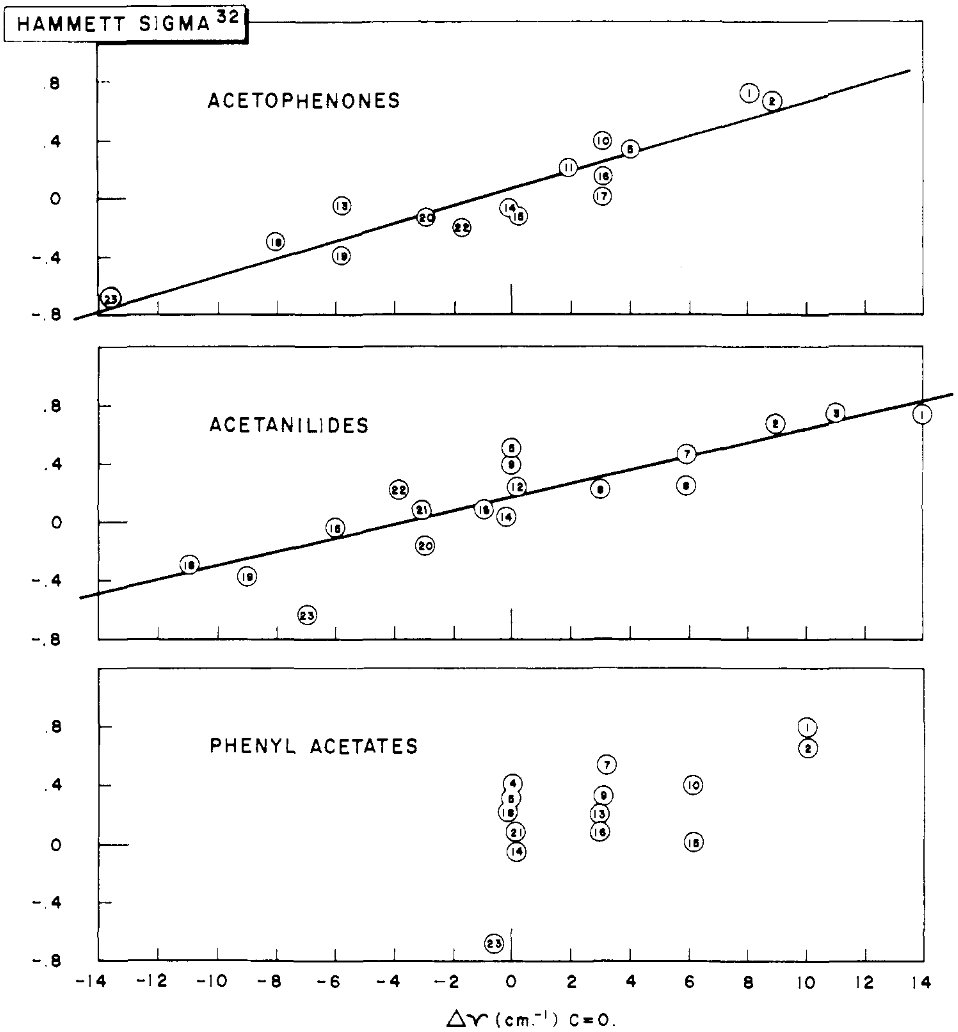

Fig. 1.—Hammett σ-constant *vs.* carbonyl frequency shift (relative to unsubstituted compound, measured in same solvent).

density at the reaction site we might expect an approximate linear relationship between the carbonyl shift and the σ-constant.[28] Such a relationship has indeed been shown to exist for benzaldehydes and acetophenones[26,29,30] and is presented here for the latter in an expanded form for both its intrinsic interest and as a background for examining a similar relationship in the acetanilides and phenyl acetates.

A detailed explanation of the electronic effect of the various substituents on the *m*- and *p*-positions of the aromatic nucleus in terms of their respective resonance and inductive effects has been given in detail by Wheland[31] for orientation in the benzene ring, Jaffé[22] and Taft[33] for σ-constants and Brown[34] for acid dissociation constants. That such an interpretation applies equally well to the aromatic carbonyl shift of acetophenone is verified by the data of Table I. Thus electron-donating substituents in the *p*-position cause a shift to lower frequency while the reverse is true of the electron-withdrawing groups in both the *m*- and *p*-position. For electron-donating groups in the *m*-position we find that the resonance-polar effect[33] predominates with *m*-amino only[35] while all other substituents in this class (no. 5, 16, 17) cause a high frequency shift, presumably due to the greater importance of the inductive (or field) effect of these groups. This is graphically illustrated in Fig. 1 in which

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(28) Deviations from an exact linear relationship may be expected inasmuch as the frequency shifts are influenced only by static factors typical of the molecule in its resting state, while σ-constants are derived from compounds which are subject to the electronic influence of the attacking reagent. This can perhaps be most clearly seen from the *p*-chloro compounds; the σ-value of the *p*-chloro group (+0.227)[32] implies that the electron density at the *p*-position is considerably decreased relative to benzene and yet the carbonyl band of both *p*-chloroacetophenone and *p*-chlorobenzaldehyde absorbs at a frequency identical to that of the parent compounds.

(29) H. W. Thompson, R. W. Needham and D. Jameson, *Spectrochim. Acta*, **9**, 208 (1957).

(30) N. Fuson, M. L. Josien and C. M. Shelton, THIS JOURNAL, **76**, 2526 (1954).

(31) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 476 ff.

(32) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(33) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chap. 13.

(34) H. C. Brown, D. H. McDaniel and O. Hafliger in "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, Chap. 14.

(35) We would expect a similar result with the *m*-methyl group in which, unlike the other *o,p*-orienting groups, the resonance and inductive effects are in the same direction. The enhanced frequency of *m*-methylacetanilide is therefore anomalous.

TABLE I

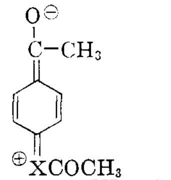
CARBONYL ABSORPTION (CM.$^{-1}$) OF SUBSTITUTED ACETOPHENONES, ACETANILIDES AND PHENYL ACETATES

No.	Substituent	Acetophenone^{a}	Acetanilide^{b}	Phenyl acetate^{a}
1	p-NO_2	1700^{22}	1712^{c}	1779
2	m-NO_2	1701^{22}	1706^{c}	1779
3	p-CN	..	1706	..
4	m-Br	..	..	1770
5	m-Cl	1696^{22}	1695	1770
6	p-Br	..	1698	..
7	p-$COCH_3$	..	1715^{a}	1773
8	p-CHO	..	1715^{a}	1773
9	m-$COCH_3$	..	1709^{*}	1773
10	m-$OCOCH_3$	1695	1709	1776
11	m-$NHCOCH_3$	1694	..	1773
12	p-$OCOCH_3$	1692	1695	1770
13	p-$NHCOCH_3$	1686	..	1764^{b}
14	H	1691^{22} 1692	1695 1709^{a} 1698^{c}	1770 1764^{b}
15	p-C_6H_5	1692	1689	1776
16	m-OCH_3	1695	1694	1773
17	m-OH	1695	..	..
18	p-OCH_3	1684^{26}	1684	1770
19	p-OH	1686^{26}	1686	..
20	m-NH_2	1689^{22}	1695^{c}	..
21	m-CH_3	..	1692	1770
22	p-CH_3	1690^{25}	1691	..
23	p-NH_2	1677^{22}	1691^{c}	1769

[a] In carbon tetrachloride. [b] In chloroform, unless otherwise noted. [c] In dioxane.

the frequency shifts of substituted acetophenones are plotted against their respective Hammett σ-constants.

Of particular significance to this study is the position of absorption of the aromatic carbonyl when influenced by a p-acetamido group in one case (no. 13) and a p-acetoxy group (no. 12) in the other. If, as postulated by others,[6,10] the abnormal carbonyl frequency of acetanilide and phenyl acetate is due to interaction of the lone-pair electrons with the benzene ring (thus decreasing their availability for interaction with the acetyl carbonyl), then this interaction should extend to the p-acetyl group as in XII and should cause



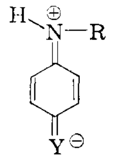
XII, X = NH or O

the carbonyl band to shift to lower frequency relative to acetophenone itself. This is indeed the case for p-acetamidoacetophenone which absorbs significantly lower and is to be contrasted with p-acetoxyacetophenone in which the aromatic carbonyl band is unchanged, thus supporting the previous conclusion that a resonance mechanism is relatively unimportant for phenyl acetate.[36]

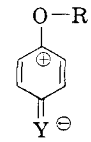
That the electron-donating ability of the p-acetamido group is small compared to its nonacylated counterpart, the p-amino group, can be seen from the absorption of p-aminoacetophenone in which the frequency decrease is over twice that of p-acetamidoacetophenone. This is attributed to (a) the increased electron affinity of the acetamide group, (b) the previously-discussed steric factors which forbid complete coplanarity of the phenyl and nitrogen planes in the p-acetamido compound but not in the p-amino, and (c) the decreased availability of the unshared nitrogen electrons in the acetamido compound due to interaction of these electrons with the amide carbonyl group. For the p-acetoxy group, factors a and b are of even greater importance and, whereas the p-methoxy group decreases the frequency of acetophenone and benzaldehyde by an average of 7 cm.$^{-1}$, we find that in the corresponding p-acetoxybenzaldehyde the frequency is actually increased by approximately 6 cm.$^{-1}$.

We may now turn our attention to the frequency shifts of the amide and ester carbonyl of substituted acetanilides and phenyl acetates, respectively (Table I). In general, we find that the frequency shifts for the acetanilides parallels those for the previously discussed acetophenones much more closely than do the phenyl acetates. This can be seen clearly from Fig. 1 where the plot of $\Delta\nu$ $vs.$ σ for the acetanilides gives a reasonably straight line,[38] but that for the phenyl acetates gives a much more random scatter with only a general drift toward higher σ-values with increasing frequency.

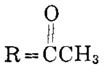
Comparison of the effect of the same substituent on the carbonyl shift of the amide and the ester indicates that the same factors cannot be equally important in both compounds. Thus we find that electron-attracting substituents (no. 1, 7 and 8) in the p-positions raise the frequency by almost twice the amount in the acetanilides. This is interpreted as substantiating the original premise that resonance is important in the amide but not in the ester. The greater frequency shift in the acetanilides is postulated as being due to the enhanced positive charge on the nitrogen arising from direct resonance interaction with the p-substituent as in XIII. In the ester, however, the positive charge at the 1-position (as in XIV) must be relayed to the carbonyl via the oxygen atom and since this is much less efficient than is the case with XIII, the frequency shift is less.



XIII



XIV



$$R = \overset{O}{\overset{\|}{C}}CH_3$$

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[36] Further corroborating evidence for this can be obtained from the recent work of Taft[37] on σ_R-constants. This constant is a direct measure of the resonance interaction of a substituent with the aromatic ring and is derived from a combination of equilibrium constant and reaction rate data. For $NHCOCH_3$, $\sigma_R = -0.22$ indicating that it is an electron-donating group of about the same magnitude as chlorine, while σ_R for acetoxy is -0.09, indicative of an extremely weak electron-donating group.

[37] R. W. Taft, Jr., N. C. Deno and P. S. Skell in "Annual Review of Physical Chemistry," Annual Reviews, Inc., Palo Alto, Calif., 1958, p. 292.

[38] No explanation can be offered for the large displacements from the curve of m-Cl (no. 5) and p-NH_2 (no. 23).

Electron-donating substituents in the *p*- or *m*-position uniformly decrease the carbonyl frequency of the acetanilides but either have no effect on, or increase the frequency of, the phenyl acetate carbonyl. The only exception to this is the very powerful electron-donating *p*-amino (no. 22) which causes a barely perceptible decrease in phenyl acetate. We must conclude from this that the greater polarizability of the nitrogen lone-pair electrons is more sensitive to the partial negative charges induced on the ring by the substituent, and thus is more efficient at relaying the effect to the C═O. It is of interest that *p*-phenyl, which does not affect the absorption frequency of acetophenone, causes a decrease of 6 cm.$^{-1}$ in acetanilide and an increase of identical value in phenyl acetate. It is well known that the phenyl group with a σ-constant of about zero may either donate or accept electrons and the complexity of the resulting situation makes further speculation unprofitable at this time.

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Kinetics of the Reduction of Nitrobenzenes by Sodium Disulfide

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The reduction of nitrobenzene by sodium disulfide to aniline has been studied kinetically at 60, 50, 40 and 30° in 70 and 40 vol. % aqueous methanolic solutions using an ultraviolet spectrophotometer. The rate was found to be proportional to the concentration of nitrobenzene and to the square of the concentration of sodium disulfide. The rate constant increased linearly with the concentration of sodium hydroxide added. The activation energy and the frequency factor of the reaction were evaluated to be 16.35 kcal. mole^{-1} and 4.57×10^8 l.^{2} mole^{-2} sec.$^{-1}$, respectively. The effect of substitutents fitted the Hammett equation well, its ρ-value being $+3.55$. The results are discussed on the standpoint of reaction mechanism involving an attack of the disulfide ion on the positive nitrogen of nitrobenzenes in conjunction with the hydrolytic equilibrium of the disulfide ion.

Although the reduction of substituted nitrobenzenes by sodium sulfides to yield the corresponding anilines is of much preparative significance, very little work has been carried out from the standpoint of reaction kinetics. The only available publication is that of Goldschmidt, *et al.*,[1] who measured the rate of sodium disulfide reduction of nitrobenzene by following the disappearance of the disulfide by acidimetry using phenolphthalein as an indicator. However, the authors' test proved this method of measurements to be unsatisfactory for deriving rate equations under various conditions.

The present study was undertaken to derive reliable rate equations, to get more information on this reaction and, if possible, to elucidate its reaction mechanism. At first, sodium monosulfide was chosen as a reducing agent, but the rates were too slow to follow the reaction kinetically. Therefore, in this study, rates of reduction of several substituted nitrobenzenes by sodium disulfide were determined spectrophotometrically using aqueous methanol as a solvent.

Experimental

Materials.—All reactants and solvents were obtained commercially or by standard methods of preparation and used after careful purification either by distillation or recrystallization. Sodium disulfide was prepared by the method of Gabel, *et al.*[2]

Isolation Experiments.—Reductions of all substituted and non-substituted nitrobenzenes were carried out under the same conditions as those of the kinetic experiments and after reaction of sufficient duration the resulting solutions were evaporated in vacuum, diluted with water, and extracted with ether. After washing with water, the ether was evaporated and the resulting anilines were, if necessary after acetylation, recrystallized and were identified by comparison with authentic specimens. Yields were in all cases above 70%.

In the case of nitrobenzene the product solution was worked up as in the kinetic experiments and its ultraviolet absorption spectrum was compared with that of an authentic solution of aniline. Coincidence was satisfactory, so that the absence of any appreciable amount of side reactions was assured.

Methods of Analysis.—The reaction was followed, at first, by electrometrical titration[3] of sodium disulfide using a standard solution of ammoniacal silver nitrate. This method of determination proved to be very accurate with sodium monosulfide but less precise with sodium disulfide. Therefore this method was used as a supplemental check of runs with a large excess of nitrobenzene, while in most of the other runs the rates were measured by following the change of ultraviolet absorption spectra of nitrobenzene (absorption maximum 270 mμ).

Typical Procedure for Rate Measurements.—An appropriate amount of methanol, water, sodium disulfide and sodium hydroxide was placed in a 100-ml. three-necked flask equipped with a reflux condenser and an outlet tube, and the flask was immersed in a thermostat regulated at definite temperatures. The reaction was commenced by introducing a definite amount of a methanolic solution of nitrobenzene previously warmed to the reaction temperature, and by thorough shaking. At appropriate time intervals aliquots (0.5 ml.) were withdrawn, poured into a 10-ml. volumetric flask containing an appropriate amount of acidic aqueous methanol (2 *N* 50 vol. % aqueous methanolic solution of sulfuric acid), diluted accurately to 10 ml. and then warmed (50°) for 5 minutes. These solutions were further diluted by acidic methanol (0.5 *N* methanolic solution of sulfuric acid) to one-tenth of its concentration, and differences of optical densities, $E_{270m\mu} - E_{245m\mu}$, of the resulting solutions were measured using a Beckman spectrophotometer, model DU. Data for a typical run[4] are given in Fig. 1.

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[1] H. Goldschmidt and H. Larsen, *Z. physik. Chem.*, **71**, 437 (1910).

[2] Y. O. Gabel and L. F. Speier, *C. A.*, **42**, 4976 (1948).

[3] H. H. Willard and F. Fenwick, THIS JOURNAL, **45**, 645 (1923).

[4] In those runs containing excess of nitrobenzene over sodium di-