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Infrared Data on the Carbonyl Group in Substituted Acetophenones

By Albert H. Soloway and S. L. Friess[1]

In an extension of a study[2] involving the reaction of meta- and para-substituted acetophenones with perbenzoic acid, it was considered of some interest to determine the characteristic infrared frequencies of the carbonyl groups in these compounds. Since previous work[2,3] indicated the existence of an ordered relationship between the nature of ring substituents present in acetophenones and the reactivity of their carbonyl function toward addition reactions, it was anticipated that a similar correlation might exist between structure-sensitive λ values for the carbonyl bands and some index of chemical reactivity of the ketone groupings.

Accordingly, a series of twelve acetophenones from the previous study with m- and p-substituents ranging in character from strongly electron-supplying to electron-withdrawing was carefully purified, and the spectrum of each member scanned over the region of the sharply defined carbonyl band. Each solid ketone was investigated as a finely ground mull in Nujol, while ketones liquid at room temperature were run directly without added solvent. The results of these infrared measurements are given in Table I, together with a tabula-

TABLE I

DATA ON MONOSUBSTITUTED ACETOPHENONES

$X - \langle C_6H_4 \rangle - COCH_3$

Substituent, X	λ (in μ) for carbonyl peak	Hammett's σ value[4] for X	Rate constant in peracid reaction,[a] (l./mole sec.) $\times 10^5$
A. Nujol mulls			
p-NH$_2$	6.12	−0.66	
p-OH	6.11		11.5[b]
p-OCH$_3$	6.03	− .27	4.42 ± 0.10
p-NHCOCH$_3$	6.02		
p-Br	6.01	+ .23	
p-OCOCH$_3$	6.00		
m-NO$_2$	5.95	+ .71	
p-NO$_2$	5.93	+1.27	
B. Pure liquids			
p-CH$_3$	5.97	−0.17	3.20 ± 0.16
m-OCH$_3$	5.95	+ .12	2.42 ± 0.18
p-Cl	5.93	+ .23	
m-Br	5.93	+ .39	

[a] Rate runs in chloroform solution of perbenzoic acid at 29.9°. Constants are given for those acetophenones which obey second order kinetics, since it is only for this type of ketone that k_2 measures carbonyl addition reactivity. [b] Value must be regarded as approximate because of a side reaction producing color in solution, presumably by nuclear attack.

(1) Naval Medical Research Institute, Bethesda, Md.
(2) S. L. Friess and A. H. Soloway, THIS JOURNAL, 73, 3968 (1951).
(3) R. P. Cross and P. Fugassi, ibid., 71, 223 (1949).

tion of Hammett's σ substituent constants[4] and a comparison column of carbonyl reactivity as measured by the rate constants for the same acetophenones in the peracid reaction.[2]

From the data of Table I it is seen that as the character of the substituent meta or para to the acetyl function changes progressively from electron-supplying to electron-withdrawing, the value of λ for the carbonyl band drops in magnitude.[5] Although the available data do not indicate a complete linear correlation between λ values and σ substituent constants, it is to be noted that a rough parallelism between these factors does exist, and that a similar degree of correspondence is found between λ values and rate-constants for the second order peracid reaction of variously substituted acetophenones.

These observations would imply that some of the same energy factors that determine a σ value for a substituent, as it affects reactivity of a functional group attached to a meta or para position, are operative in altering fundamental vibrational frequencies within groups at these positions.

Experimental

Small samples of the acetophenones previously purified for rate work[2] were either recrystallized or redistilled before scanning of their infrared spectra.[6]

Sample and blank tracings were obtained using a Perkin–Elmer single beam recording infrared spectrometer (model 12 AB), at maximum sensitivity over a 2 μ range including the carbonyl band. A cell of 0.025 mm. thickness was used in all runs.

(4) For σ values as indices of relative electron supply or withdrawal see L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, Chap. 7.

(5) For a similar effect on the carbonyl band of unconjugated esters, in which electronegative α-substituents like the acetoxy or the cyano group cause a lowering of the wave length for carbonyl stretching relative to that for the unsubstituted ester, see R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, 71, 1073 (1949).
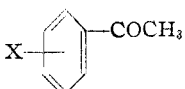
(6) We are indebted to Mr. Carl Whiteman for obtaining the machine tracings in all runs.

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Organic Peracid–Sodium Bisulfite Mixtures as Acylating Agents[1]

By A. H. Soloway[2] and S. L. Friess[3]

In the course of work on the peracid degradation of certain aromatic ethers, it was observed that either aqueous peracetic acid solution or dilute aqueous perbenzoic acid solution, upon treatment with sodium bisulfite in the usual procedure to destroy the oxidizing power of the peracid, results in a solution which contains an active acylating agent for certain amines. Each amine which does react with the peracid–bisulfite mixture furnishes a single product in good yield via the over-all reaction.

$$RCO_3H \xrightarrow[\text{2, R'NH}_2]{\text{1, NaHSO}_3} RCONHR'$$

$$R = CH_3, C_6H_5$$
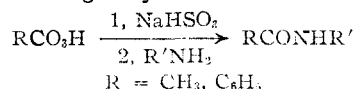
(1) This work was supported in part by a Frederick Gardner Cottrell grant from the Research Corporation.
(2) Beaunit Mills Fellow in Chemistry, 1950–1951.
(3) Naval Medical Research Institute, Bethesda, Md.

Table I presents a compilation of reaction conditions employed and products and yields obtained in a set of test runs on various common amines, and notes by a zero yield those amines which failed to react under the given conditions. In all reactions, a large excess of both 10% sodium bisulfite reagent and of the amine were used, with the peracid present in limiting amount. In general, the amide product obtained directly from a reaction mixture was quite pure.

Table I

Amine or hydrazine	Peracid, R =	—Moles of reactants— Amine	Peracid	NaH SO₃	Amide product Yield,[c] %	M.p.,[d] °C.
Aniline	C₆H₅	0.011	0.00108	0.018	80	160–162
Aniline	CH₃[a]	.010	.00246	.040	86	113–114
Aniline	CH₃[b]	.011	.00500	.014	64	113–114
m-ClC₆H₄NH₂	C₆H₅	.0039	.00108	.018	46	118–119
Piperidine	C₆H₅	.012	.00122	.018	0	
N-Methylaniline	C₆H₅	.0093	.00108	.018	0	
Methylamine[f]	C₆H₅	.048	.00120	.018	0	
n-Butylamine	C₆H₅	.014	.00110	.014	0	
C₆H₅NHNH₂	C₆H₅	.0092	.00108	.018	79	166–168[e]
C₆H₅NHNH₂	CH₃[a]	.0092	.00246	.027	69	127–128[e]
Cyclohexylamine	C₆H₅	.010	.00110	.018	45	147–148

[a] Stock solution prepared by the method of T. W. Findley, D. Swern and J. T. Scanlan, This Journal, 67, 412 (1945); aliquots diluted with water before use. [b] Prepared by dilution of a 40% solution, kindly furnished by The Buffalo Electro-Chemical Company, Inc. [c] Yield of crude amide, based on peracid. [d] All melting points were undepressed on admixture with authentic samples of the respective amides. [e] The amides isolated were the β-aroyl and acyl derivatives. [f] A 25% aqueous amine solution was used.

The data of Table I indicate the general utility of peracid–bisulfite mixtures in acetylating or benzoylating primary aromatic amines or hydrazines, with cyclohexylamine also undergoing the reaction successfully. Complete failure (under the applied conditions) of this acylation process for the primary aliphatic amines and for the single secondary aromatic amine tested is to be noted.

Curiously, these results in part parallel those found by Tarbell and Noble[4] in a study of the benzoylating power of thiobenzoic acid. It was observed that aniline readily furnished benzanilide on being treated at room temperature with thiobenzoic acid, but no amide could be isolated from attempted reaction with either piperidine or methylaniline. This parallelism at least raises the possibility that the active acylating agent resulting from peracid–bisulfite interaction possesses a carbonyl–sulfite linkage, at some stage of its formation or use.

Experimental

The amines tested in these reactions, with the exception of methylamine, were purified before use by distillation. Chloroform solutions of perbenzoic acid were prepared according to Braun.[5]

In a reaction typical of those given for perbenzoic acid in Table I, a 100-ml. portion of a ca. 0.4 M chloroform solution of the peracid was extracted with a 60-ml. volume of ice-cold water. A one-ml. aliquot of the aqueous extract was titrated iodometrically[5] to determine its peracid concentration. A 50-ml. portion of this extract was then reduced with excess 10% aqueous sodium bisulfite solution, and the mixture cooled in an ice-bath. To this solution was then added with swirling a calculated excess of the pure amine (without diluent), and the resulting mixture allowed to stand for one hour at room temperature.

(4) P. Noble, Jr., Ph.D. Thesis, University of Rochester, 1950.

(5) G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 434.

Generally, a successful reaction of an amine with peracid–bisulfite was very rapid, with the amide separating from solution almost instantaneously. To ensure completeness of reaction, each mixture was allowed to stand for an hour before the product was filtered and recrystallized.

In runs employing peracetic acid, no preliminary extractions were needed. Addition of the bisulfite, and the remainder of the above procedure were applied directly to a stock peracid aliquot diluted with cold water.

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Mass Spectrometric Analysis of Deuterated Hydrocarbons

By A. W. Tickner, W. A. Bryce and F. P. Lossing

In a recent paper Stevenson and Wagner[1] have presented several methods for determining the amount of undeuterated paraffins present in monodeuteroparaffins. Because of the increasing importance of deuterium-substituted hydrocarbons in kinetic studies, it seemed of interest to investigate the applicability of methods of this type to the general problem of analyzing mixtures of deuterated hydrocarbons.

The methods described by Stevenson and Wagner are based on measurements of mass spectra at low ionizing electron energies and involve the assumption that the appearance potentials of corresponding monodeuterated and undeuterated ions differ only due to differences in zero point energy which are estimated at 0.02–0.05 e.v. An investigation in this Laboratory, which is the subject of a separate communication,[2] has shown that the ionization potentials of the deuterated methanes, as measured by electron impact, differ considerably from one another. The difference in ionization potential between CH_4 and the various deuterated methanes was found to increase with the extent of deuteration from 0.04 ± 0.02 e.v. for CH_3D to 0.18 ± 0.02 e.v. for CD_4. Thus it appears that, while the limits of error estimated by Stevenson and Wagner for their determination of CH_4 in CH_3D are adequate, using the above procedures as general methods of analysis for mixtures of the deuterated methanes might result in much larger errors.

In order to estimate the size of the errors to be encountered in analyzing mixtures of deuterated methanes at reduced electron energies, known mixtures were prepared. Monodeuteromethane was made by the method of Childs and Jahn[3] and the CD_4 by the method of Urey and Price.[4]

Analysis of the CH_3D at low electron energies (see ref. 1, p. 5615) showed that it contained 2.7 ± 0.3% CH_4. Analysis of the CD_4 at low electron energies showed the presence of 4.7 ± 0.1% CHD_3, while the mass spectrum at 50 volts gave 4.66 ± 0.03% CHD_3. Mixtures of these methanes with CH_4 were analysed by scanning the mass spectrum at low electron accelerating voltages. The energy of ionizing electrons was decreased until only

(1) D. P. Stevenson and C. D. Wagner, This Journal, 72, 5612 (1950).

(2) F. P. Lossing, A. W. Tickner and W. A. Bryce, J. Chem. Phys., in press.

(3) W. H. J. Childs and H. A. Jahn, Proc. Roy. Soc. (London), A169, 428 (1939).

(4) H. C. Urey and D. Price, J. Chem. Phys., 2, 300 (1934).