gratefully a grant from The Royal Society for the purchase of N^{15}. This work was performed during the tenure of a Royal Scholarship by (J.H.S.).

DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY
LONDON, S. W. 7
RECEIVED APRIL 26, 1951

Infrared Data on the Carbonyl Group in Substituted Acetophenones

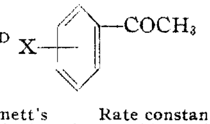
BY ALBERT H. SOLOWAY AND S. L. FRIESS[1]

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 tabulation 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]

TABLE I

DATA ON MONOSUBSTITUTED ACETOPHENONES



Substituent, X	λ (in μ) for carbonyl peak	Hammett's σ value[4] for X	Rate constant in peracid reaction,[a] (l./mole sec.) × 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.

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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER 3, NEW YORK, AND THE
NAVAL MEDICAL RESEARCH INSTITUTE
BETHESDA 14, MARYLAND
RECEIVED JUNE 6, 1951

---

[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).

[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.

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.

$$\mathrm{RCO_3H} \xrightarrow[2,\ \mathrm{R'NH_2}]{1,\ \mathrm{NaHSO_3}} \mathrm{RCONHR'}$$
$$\mathrm{R = CH_3,\ C_6H_5}$$

---

[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.