[CONTRIBUTION FROM THE DEPARTMENTS OF PHYSICS AND CHEMISTRY, FISK UNIVERSITY]

An Infrared Spectroscopic Study of the Carbonyl Stretching Frequency in Some Groups of Ketones and Quinones

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The infrared spectra of over one hundred ketones and quinones have been measured in the six μ region. The position of the carbonyl band is discussed as a function of one or more of the following: C=C conjugation, proximity of a cyclopropane ring, length of the aliphatic chain, branching of the chain, ring strain, Hammett's substituent constant and oxidation-reduction potential. These results extend the scope of a study, being carried on in this Laboratory, of the effect of molecular environment upon the carbonyl frequency.

Introduction

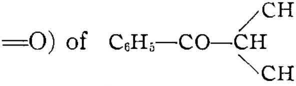
During recent years a very active interest has been taken in small variations of the carbonyl bond stretching frequency in the infrared spectrum of groups of similar ketones and quinones. These studies have proved useful not only for compound identification purposes but also in order to obtain by experimental means a measure of particular factors in the molecular environment which have been predicted theoretically on a qualitative basis[1–14] as well as on a quantitative basis.[15,16] A more complete survey of the literature has been given elsewhere.[12,13] The results obtained in this Laboratory thus far[12,13] have shown that ν(C=O) may be correlated with molecular structure and bond order. The new results in this present paper include measurements, on several very different sets of molecules, which will both enlarge the experimental basis for conclusions previously drawn, and present additional experimental data upon which more theoretical calculations can be based.

Experimental

The spectrometer used in this study was a single beam automatic recorder equipped with a large rock salt prism.[17] Reproducibility was such that sharp bands between 1600 and 1800 cm.$^{-1}$ could be measured to within ±1 cm.$^{-1}$ or ±2 cm.$^{-1}$.[13] Since intermolecular bonding effects and solvent interaction effects are so frequent for samples run in the solid state and in polar solvents, respectively, sample spectra were obtained in dilute carbon tetrachloride solution. The only exceptions were the diphenoquinones which, being in some cases insoluble in carbon tetrachloride, were studied in chloroform solution. The thickness of the absorption cell employed was usually 1 mm. It was necessary to use 2-mm. and 3-mm. cells for some of the less soluble compounds.

Discussion

The results are presented in Table I. Each group of compounds will be discussed below in the order in which they appear in the table.

A. Phenyl Ketones and Styryl Ketones.—In a study of some phenyl ketones Mariella and Raube have shown that the cross conjugation effect upon the *ultraviolet* spectra is "damped out" for all but phenyl propenyl ketone.[18] In contrast to this, we have found that the *infrared* carbonyl stretching frequency of compounds of the type C_6H_5–CO–X is markedly sensitive to changes in the substituent, decreasing with different X-substituents in the following order: saturated straight chain (XLI through XLVIII), 1691 ± 1 cm.$^{-1}$; cyclanes with more than three carbons in the ring (III, IV, V), 1686 ± 1 cm.$^{-1}$; $-CH=CH-CH_3$ (I), 1680 cm.$^{-1}$; cyclopropane (II), 1677 cm.$^{-1}$; and the phenyl group (LXXXI), 1664 cm.$^{-1}$. While the infrared ν(C=O) of  $C_6H_5-CO-CH\begin{smallmatrix}\diagup CH_2\\ \diagdown CH_2\end{smallmatrix}$ and that of $C_6H_5-CO-C=C-$ are shifted by different amounts, the ultraviolet spectra[18] for these are identical. This is in contrast to the steroid case where the shifting effect of cyclopropane upon *both* ultraviolet[19] and infrared[5] spectra is less than that of the unsaturated C=C link.

The shifting effects of the cyclopropane ring upon the position of ν(C=O) in phenyl ketones is slightly larger than that of the –C=C– group. This is the reverse of the situation found when the carbonyl carbon is a member of a 6-carbon ring, *i.e.*, unconjugated 3-ketone steroids,[1] 1719 ± 1 cm.$^{-1}$; *i*-cholestane-6-one,[17] *i*-androstandione,[17] and carone,[12] 1689 ± 2 cm.$^{-1}$; conjugated 3-ketone steroids,[1] 1677 ± 3 cm.$^{-1}$.

The effect of the X-substituent of the $C_6H_5-CH=CH-CO-X$ group upon the carbonyl frequency is less easy to determine than in the previous case. The introduction of the conjugated C=C group in each compound adds another absorption band in the 1600 cm.$^{-1}$ region and in two of the six cases we studied we were not able to resolve the ν(C=C) and the ν(C=O) bands. Nevertheless it is

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[1] R. N. Jones, V. Z. Williams, M. J. Whalen and K. Dobriner, THIS JOURNAL, **70**, 2024 (1948).

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

[3] R. S. Rassmussen, D. D. Tunicliff and R. R. Brattain, THIS JOURNAL, **71**, 1068 (1949).

[4] I. M. Hunsburger, *ibid.*, **72**, 5626 (1950).

[5] M. L. Josien and N. Fuson, *Compt. rend.*, **231**, 1511 (1950).

[6] M. L. Josien and N. Fuson, THIS JOURNAL, **73**, 478 (1951).

[7] N. J. Leonard, H. S. Gutowsky, W. J. Middleton and E. M. Peterson, *ibid.*, **74**, 4070 (1952).

[8] G. R. Clemo and D. G. I. Felton, *J. Chem. Soc.*, 1658 (1952).

[9] I. M. Hunsburger, R. Ketcham and H. S. Gutowsky, THIS JOURNAL, **74**, 4839 (1952).

[10] E. D. Bergmann and S. Pinchas, *J. chim. phys.*, **49**, 537 (1952).

[11] M. L. Josien, N. Fuson and D. E. Pearson, *Compt. rend.*, **235**, 1206 (1952).

[12] M. L. Josien and N. Fuson, *Bull. soc. chim. France*, **19**, 389 (1952).

[13] M. L. Josien, N. Fuson, J. M. Lebas and T. M. Gregory, *J. Chem. Phys.*, **21**, 331 (1953).

[14] M. L. Josien and N. Fuson, *Compt. rend.*, **236**, 1879 (1953).

[15] G. B. Bonino and E. Scrocco, *Atti. Nazl. Lincie, Rend., Classe sci. fis.*, **6**, 421 (1949, XIII); **8**, 183 (1950, VIII); E. Scrocco and P. Chiorboli, *ibid.*, **8**, 248 (1950, VIII).

[16] G. Berthier, B. Pullman and J. Pontis, *J. chim. phys.*, **49**, 367 (1952).

[17] M. L. Josien, N. Fuson and A. S. Cary, THIS JOURNAL, **73**, 4445 (1951).

[18] R. P. Mariella and R. R. Raube, *ibid.*, **74**, 518 (1952).

[19] I. M. Klotz, *ibid.*, **66**, 88 (1944).

clear that the ν(C=O) of the styryl ketones when X is the cyclopropane ring (IX), (1685 cm.$^{-1}$), is not as high as when the X-substituents are cyclanes with more than three carbons in the ring (X and XI), (1690 ± 1 cm.$^{-1}$). There is definite indication that ν(C=O) for the saturated straight chain substituent (VI) is still higher (*ca.* 1695 cm.$^{-1}$). The substitution of the styryl group for the phenyl group in each case raises the carbonyl frequency by about 5 cm.$^{-1}$.

B. Cyclopentenones and Cyclohexenones.—Because of previous studies made by Jones, *et al.*,[1] and Leonard, *et al.*,[7] we thought it would be of interest to make an infrared study of the set of

TABLE I

CARBONYL FREQUENCIES OF SEVERAL SETS OF KETONES AND QUINONES, TABULATED IN SOME CASES WITH THE CORRESPONDING HAMMETT'S CONSTANTS, OXIDATION–REDUCTION POTENTIALS, AND/OR ULTRASONIC VELOCITIES

Number	Name	Source[a]	ν(C=O),[b] cm.$^{-1}$	Other data as indicated ν(C=C), cm.$^{-1}$
	A. Phenyl and styryl ketones			
I	Phenyl propenyl ketone	1	1680	
II	Phenyl cyclopropyl ketone	1	1677	
III	Phenyl cyclobutyl ketone	1	1686	
IV	Phenyl cyclopentyl ketone	1	1687	
V	Phenyl cyclohexyl ketone	1	1686	
VI	Styryl propyl ketone	1	(1710–1670)[c]	
VII	Styryl isopropyl ketone	1	1692	1669
VIII	Styryl isobutyl ketone	1	(1700–1660)[c]	
IX	Styryl cyclopropyl ketone	1	1685	1662
X	Styryl cyclobutyl ketone	1	1691	1667
XI	Styryl cyclohexyl ketone	1	1690	1663
	B. Cyclopentenones and cyclohexenones			
XII	4-Hydroxy-4,3-diphenyl-2-methyl-Δ^2-cyclopentenone	2	1712	
XIII	4-Hydroxy-4,3-diphenyl-Δ^2-cyclopentenone	2	1720	
XIV	5-Benzylidene-3-methyl-2-propyl-Δ^2-cyclopentenone	2	1694	
XV	5-Benzylidene-3-phenyl-Δ^2-cyclopentenone	2	1699	
XVI	5-Benzylidene-4-hydroxy-4,3-diphenyl-Δ^2-cyclopentenone	2	1697	
XVII	5-Benzylidene-4-hydroxy-4,3-diphenyl-2-methyl-Δ^2-cyclopentenone	2	1699	
XVIII	5-Benzylidene-4-hydroxy-4,3,2-triphenyl-Δ^2-cyclopentenone	2	1702	
XIX	5-Isopropylidene-4-hydroxy-4,3-diphenyl-Δ^2-cyclopentenone	2	1688	
XX	2,3,6,7-Tetraphenyl-$\Delta^{2,6,8}$-cycloindatrienone	2	1690	
XXI	6-Benzylidene-5,3-dimethyl-Δ^2-cyclohexenone	2	1664	
XXII	6-Benzylidene-5,5,3-trimethyl-Δ^2-cyclohexenone	2	1664	
	C. Tocopherylquinones			
XXIII	α-Tocopherylquinone	3	1641	
XXIV	β-Tocopherylquinone	3	1649	
				E,[d] volt
	D. Methyl-1,2-benzanthraquinones			
XXV	1,2-Benzanthraquinone	4	1670	0.224
XXVI	3-Methyl-1,2-benzanthraquinone	4	1670	.208
XXVII	4-Methyl-1,2-benzanthraquinone	4	1670	.177
XXVIII	5-Methyl-1,2-benzanthraquinone	4	1668	.168
XXIX	6-Methyl-1,2-benzanthraquinone	4	1670	.211
XXX	7-Methyl-1,2-benzanthraquinone	4	1670	.209
XXXI	2'-Methyl-1,2-benzanthraquinone	4	1670	.213
XXXII	3'-Methyl-1,2-benzanthraquinone	4	1670	.213
XXXIII	4'-Methyl-1,2-benzanthraquinone	4	1671	.209
XXXIV	5,6-Dimethyl-1,2-benzanthraquinone	4	1668	
XXXV	6,7-Dimethyl-1,2-benzanthraquinone	4	1670	.200
	E. Diphenoquinones			
XXXVI	Diphenoquinone (red form)	5	1635	
XXXVII	Diphenoquinone (gold form)	5	1635	
XXXVIII	3,5,3',5'-Tetramethyldiphenoquinone	5	1637	
XXXIX	3,5,3',5'-Tetra-*t*-butyldiphenoquinone	5	1634	
XL	3,5,3',5'-Tetrachlorodiphenoquinone	5	1646	

TABLE I (*Continued*)

Number	Name	Source[a]	ν(C=O),[b] cm.$^{-1}$	Other data as indicated *V*,[e] m. sec.$^{-1}$	
	F. Alkyl phenyl and *p*-xylyl alkyl ketones				
XLI	Methyl phenyl ketone (acetophenone)	6	1692	1463	
XLII	Ethyl phenyl ketone	6	1692	1456	
XLIII	Butyl phenyl ketone	6	1690	1434	
XLIV	Amyl phenyl ketone	6	1690	1433	
XLV	Hexyl phenyl ketone	6	1690	1436	
XLVI	Heptyl phenyl ketone	6	1690	1437	
XLVII	Octyl phenyl ketone	6	1691	1445	
XLVIII	Nonyl phenyl ketone	6	1690	1451	
XLIX	Methyl *p*-xylyl ketone	6	1690	1445	
L	Ethyl *p*-xylyl ketone	6	1691	1434	
LI	Propyl *p*-xylyl ketone	6	1689	1420	
LII	Butyl *p*-xylyl ketone	6	1690	1414	
LIII	Amyl *p*-xylyl ketone	6	1690	1414	
LIV	Hexyl *p*-xylyl ketone	6	1690	1416	
LV	Heptyl *p*-xylyl ketone	6	1690	1421	
LVI	Octyl *p*-xylyl ketone	6	1689	1428	
LVII	Nonyl *p*-xylyl ketone	6	1690	1430	
				E,[f] volt	
	G. Alkyl alkyl ketones				
LVIII	2-Propanone (methyl methyl)	7	1719	0.129	
LIX	2-Butanone (methyl ethyl)	7	1720	.123	
LX	3-Methyl-2-butanone (methyl isopropyl)	7	1718	.122	
LXI	2-Pentanone (methyl propyl)	8	1720	.122	
LXII	4-Methyl-2-pentanone (methyl isobutyl)	7	1720	.122	
LXIII	2-Heptanone (methyl amyl)	7	1719	.121	
LXIV	3-Pentanone (ethyl ethyl)	7	1717	.118	
LXV	3-Hexanone (ethyl propyl)	6	1718	.117	
LXVI	3-Heptanone (ethyl butyl)	6	1717	.116	
LXVII	3-Octanone (ethyl amyl)	6	1717	.117	
LXVIII	2-Heptanone (propyl propyl)	6, 7	1716	.110	
LXIX	2,4-Dimethyl-2-pentanone (di-isopropyl)	6	1713	.109	
LXX	4-Nonanone (propyl amyl)	6	1715	.109	
LXXI	5-Nonanone (butyl butyl)	6, 7	1716	.101	
LXXII	5-Decanone (butyl amyl)	6	1715	.103	
LXXIII	6-Undecanone (amyl amyl)	6	1716	.095	
				Additional (C=O), cm.$^{-1}$	
	H. Epoxy ketones				
LXXIV	1,4-Naphthoquinone		1675[g]		
LXXV	1,4-Naphthoquinone-2,3-oxide	10	1710		
LXXVI	Progesterone[h]	11	1707	1681[i]	
LXXVII	Oxido-progesterone	11	1709	1680[i]	
LXXVIII	Pregnenolone acetate	11	1708	1738[j]	
LXXIX	Oxido-pregnenolone acetate	11	1705	1748[j]	
				E,[k] volt	σ[l]
	I. Substituted benzophenones				
LXXX	4,4′-Di-(dimethylamino)-benzophenone	9	1639		
LXXXI	4-Aminobenzophenone	9	1651	−1.161	−0.66
LXXXII	4,4′-Dimethoxybenzophenone	9	1655	−1.260	− .536
LXXXIII	4,4′-Dimethylbenzophenone	9	1659	−1.187	− .340
LXXXIV	4-Methoxybenzophenone	9	1658	−1.194	− .268
LXXXV	4-*t*-Butylbenzophenone	9	1664	−1.166	− .197
LXXXVI	4-Methylbenzophenone	9	1661	−1.165	− .170
LXXXVII	Benzophenone	9	1664	−1.140	.0
LXXXVIII	4-Chloro-4′-methylbenzophenone	9	1667	−1.102	.057
LXXXIX	4-Chlorobenzophenone	9	1666	−1.093	.227
XC	4-Bromobenzophenone	9	1665	−1.051	.232
XCI	3-Bromobenzophenone	9	1669	−1.021	.391
XCII	4,4′-Dichlorobenzophenone	9	1670	−1.002	.454
XCIII	3,3′-Dibromobenzophenone	9	1672	−0.913	.782

TABLE I (*Continued*)

Number	Name	Source[a]	$\nu(C{=}O)$,[b] cm.$^{-1}$	Other data as indicated σ^m
	J. Substituted acetophenones			
XCIV	*p*-Aminoacetophenones	12	1677	−0.66
XCV	*p*-Hydroxyacetophenone	12	1686	− .317
XCVI	*p*-Methoxyacetophenone	12	1684	− .268
LXI	Acetophenone	6	1692	.0
XCVII	*p*-Chloroacetophenone	12	1692	.227
XCVIII	*p*-Bromoacetophenone	12	1693	.232
XCIX	*m*-Nitroacetophenone	12	1701	.710
C	*p*-Nitroacetophenone	12	1702	.778[n]
CI	*p*-Acetoxyacetophenone	12	1691	
CII	*p*-Acetylaminoacetophenone	12	1686	

[a] (1) R. P. Mariella, Loyola Univ., Chicago, Ill. (compounds re-purified by C. M. Hill, Tenn. A & I State Univ., Nashville, Tenn.). (2) H. S. French, Wellesley College, Wellesley, Mass. (compounds re-purified by C. M. Hill, Tenn. A & I State Univ., Nashville, Tenn.). (3) M. Farber, Cornell Univ. Medical College, New York, N. Y. (4) J. Iball, University College, Dundee, Scotland. (5) H. Hart, Michigan State College, E. Lansing, Mich. (6) R. T. Lagemann, Vanderbilt Univ., Nashville, Tenn. (7) Commercial product (Fisher Scientific Co.). (8) Commercial product (Eastman Kodak Co.). (9) D. E. Pearson, Vanderbelt Univ., Nashville, Tenn. (10) L. F. Fieser, Harvard Univ., Cambridge, Mass. (11) P. L. Julian, Research Dept., Soya Products Division of the Glidden Co., Chicago, Ill. (12) A. H. Soloway, Sloan–Kettering Institute for Cancer Research, New York, N. Y. [b] All frequencies were measured for compounds in dilute solution in carbon tetrachloride with the exception of the diphenoquinones which were studied in dilute chloroform solution. [c] The C=O and C=C absorption bands were not sufficiently resolved in this case to justify assigning frequencies. The numbers in parentheses give the general location and width of the unresolved doublet. [d] Oxidation–reduction potentials taken from ref. 22. [e] Ultrasonic velocities taken from ref. 24. [f] Oxidation–reduction potentials taken from ref. 26. [g] Carbonyl frequency taken from ref. 13. [h] Dilute CS_2 solution frequencies of 1708 and 1677 cm.$^{-1}$ are given for this compound in ref. 1. [i] This lower frequency of the pair is assigned to the conjugated 3-keto carbonyl group (see ref. 1). [j] This higher frequency of the pair is assigned to the acetate $\nu(C{=}O)$ (see ref. 1). [k] Oxidation–reduction potentials taken from ref. 30. [l] Hammett substituent constants taken from ref. 31, p. 188. C. C. Price and D. C. Lincoln, THIS JOURNAL, **73**, 5836 (1951), confirm the *p*-methyl and *p*-*t*-butyl values almost exactly. [m] Hammett substituent constants taken from ref. 31 except that for *p*-hydroxy which is as calculated by Jaffe in ref. 35. No values of σ were found for *p*-acetoxy or *p*-acetylamino. [n] Hammett (ref. 31, p. 188) lists two σ-values for the *p*-nitro substituent. The value used here is the one which he states is "for all benzene derivatives except those of aniline and phenol."

cyclopentenones and cyclohexenones recently studied in the ultraviolet by French.[20] They proved to be a good example of the sensitivity of the infrared carbonyl frequency to molecular structure. The carbonyl frequency of the *endo*-conjugated cyclopentenones (XII and XIII) (1716 ± 4 cm.$^{-1}$) is close to the value of 1716 cm.$^{-1}$ found for α,β-conjugated cyclopentenones.[1] Of the *endo*- and *exo*-conjugated cyclopentenones those in which the *exo*-unsaturated bond terminates in a C_6H_5 group (XIV through XVIII) have a carbonyl frequency of 1698 ± 4 cm.$^{-1}$, that for the two others not having the benzene ring termination (XIX and XX) being 1689 ± cm.$^{-1}$. Finally the carbonyl frequency of the *endo*- and *exo*-conjugated cyclohexenones (XXI and XXII) is 1664 cm.$^{-1}$.

C. Tocopherylquinones.—Rosenkrantz and Milhorat[21] made an infrared study of tocopherylquinones in the solid state. They suggested that the low values of $\nu(C{=}O)$ which they found were a result of hydrogen bonding. This would require a chelation effect resulting from the formation of an eight-atom ring, an effect which has not yet been substantiated in the literature. We have been able to obtain relatively sharp bands at 1641 and 1649 cm.$^{-1}$ for α-tocopherylquinone and β-tocopherylquinone, respectively, in carbon tetrachloride solution. These bands, which we have assigned to $\nu(C{=}O)$, appear to be free from overlap with $\nu(C{=}C)$ bands. We disagree with Rosenkrantz's hypothesis, suggesting rather that these low frequencies are produced by an induction effect resulting from the large number of substituents attached directly to the quinone ring itself. An example of the strong effect of substituents on the quinone ring is to be found[13] in the following series: 1,4-naphthoquinone (1675 cm.$^{-1}$); 2,3-dimethyl-1,4-naphthoquinone (1660 cm.$^{-1}$), $\Delta\nu = -15$ cm.$^{-1}$; and 2,3-dichloro-1,4-naphthoquinone (1687 cm.$^{-1}$), $\Delta\nu = +12$ cm.$^{-1}$. For a corresponding 1,4-benzoquinone series with four substituents on the quinone ring, one might predict, by analogy, that the frequency shifts should be about double those for the 2,3-disubstituted naphthoquinone ring. This suggestion is borne out experimentally,[13] for the frequency shift from 1,4-benzoquinone (1667 cm.$^{-1}$) to 2,3,4,5-tetrachlorobenzoquinone (1695 cm.$^{-1}$) is $\Delta\nu = +28$ cm.$^{-1}$. Thus we predict that the frequency of 2,3,5,6-tetramethylbenzoquinone should be *ca.* 1667 − (2 × 15) or *ca.* 1637 cm.$^{-1}$,[21a] and that the frequency of 2,3,5-trimethylbenzoquinone, decreased about 75% as much, should be *ca.* 1645 cm.$^{-1}$. The α- and β-tocopherylquinones, which are rather similar to tetramethyl- and trimethyl-1,4-benzoquinones, have frequencies (1641 and 1649 cm.$^{-1}$, respectively) which are thus quite close to those predicted.

D. Methyl Benzanthraquinones.—The variation in oxidation–reduction potential is very small for the set of methyl benzanthraquinone isomers studied by Iball.[22] Table I shows that for these compounds $\nu(C{=}O)$ is if anything an increasing

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[20] H. S. French, THIS JOURNAL, **74**, 514 (1952).

[21] H. Rosenkrantz and A. T. Milhorat, *J. Biol. Chem.*, **187**, 83 (1950).

[21a] One of us (M. L. J.) recently obtained some 2,3,4,5-tetramethylbenzoquinone from Dr. Souchay of the Sorbonne. Its $\nu(C{=}O)$ (measured at the Université de Bordeaux) is 1641 cm.$^{-1}$. This fits rather closely our prediction.

[22] J. Iball, *Am. J. Cancer*, **38**, 372 (1940).

function of the oxidation–reduction potential, although the shifts in ν(C=O) are likewise too small to be used as a basis upon which to make any precise correlation.

E. Diphenoquinones.—Detroit and Hart's recent study of the effect of substitution on the ultraviolet absorption spectrum of diphenoquinone[23] stimulated us to make a parallel infrared study. Diphenoquinone in the solid state exists in two crystalline modifications,[23] the red modification being much more soluble in chloroform than the gold. (We found the Nujol mull spectra of the two forms to be practically identical.) Diphenoquinone itself and some of the substituted diphenoquinones being insoluble in non-polar solvents such as carbon tetrachloride and carbon disulfide, all this group of compounds were run in the polar solvent, chloroform. Jones, *et al.*,[1] have shown for steroids that chloroform solution carbonyl frequencies ranged from 0 to 22 cm.$^{-1}$ lower than the corresponding carbon tetrachloride solution frequencies. Similar results have been recorded for quinones.[12] The amount of the shift is as yet unpredictable. Thus it is not possible to draw significant conclusions between the chloroform solution diphenoquinone results and carbon tetrachloride solution spectra of other groups of compounds containing the carbonyl group. It is very possible, also, that chloroform solution frequencies of the different substituted diphenoquinones are variously effected by interaction with the polar solvent. With the preceding statement in mind as a reservation, it may be pointed out that the carbonyl frequency of diphenoquinone (XXXVI and XXXVII) (1635 cm.$^{-1}$) is not shifted when the hydrogens on the four carbons adjacent to the carbonyl groups are replaced by methyl or *t*-butyl groups. The tetrachloro substitution, however, increases the frequency by 11 cm.$^{-1}$.

F. Alkyl Phenyl Ketones and *p*-Xylyl Alkyl Ketones.—Lagemann, *et al.*,[24] have recently shown that the ultrasonic velocity in a series of alkyl phenyl ketones passes through a minimum for amyl phenyl ketone. They found that this minimum velocity also occurs for the same alkyl chain length in *p*-xylyl alkyl ketones. A study of the infrared spectrum of these two series of compounds shows that the carbonyl frequency of the former series (XLI–XLVIII) is constant at 1691 ± 1 cm.$^{-1}$, that of the latter series (XLIX–LVII) being constant at 1690 ± 1 cm.$^{-1}$. Thus the carbonyl frequency remains unaffected by the peculiarity of these two series of molecules, whatever it is, which is responsible for the appearance of the ultrasonic minima.

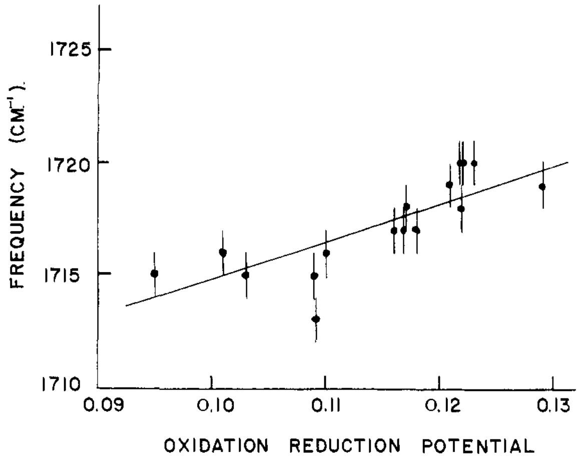

Fig. 1.—Carbonyl frequency *vs.* oxidation–reduction potential for alkyl alkyl ketones in carbon tetrachloride solution.

G. Alkyl Alkyl Ketones.—Syrkin and Dyatkina state that "in a series of saturated ketones the value for the (carbonyl) frequency of 1710 cm.$^{-1}$ remains constant irrespective of the chain length. . ."[25] Figure 1 is a graph of the ν(C=O) of the alkyl alkyl ketones obtained in this study *vs.* the corresponding oxidation–reduction potentials.[26] The ν(C=O) is, again, an increasing function of the potentials, the slope of the curve being about 2 cm.$^{-1}$/centivolt. This result shows that Syrkin and Dyatkina's statement should be considered as only a first approximation, useful when comparing saturated ketone frequencies with other carbonyl frequencies. Our results in Table I show that for a symmetrical chain ketone ν(C=O) decreases from 1719 cm.$^{-1}$ for methyl methyl ketone (LVIII) to 1715 cm.$^{-1}$ for amyl amyl ketone (LXXIII) as the chain length increases. Because of the small frequency shift we would not put as much emphasis upon this result as we have if it had not been for the rather large number of ketones available, thus giving statistical weight to the study.

An examination of Hartwell, Richards and Thompson's vapor data on some of these compounds[2] shows that in the vapor state the decrease in ν(C=O) for the long chain ketones is 9 cm.$^{-1}$ this being larger than the corresponding decrease in the solution state. This is to be expected because of the dielectric constant effect.[27] For the non-symmetrical methyl alkyl ketone series (LVIII–LXIII) the ν(C=O) in solution appears to be constant at 1719 cm.$^{-1}$ as the chain increases. Hartwell, *et al.*,'s data for gaseous CH_3–CO–R ketones show a decrease of 4 cm.$^{-1}$ as R increases from $-CH_3$ to $-(CH_2)_3CH_3$. Since this is about half that for the symmetrical gaseous ketones, by analogy, the shift in the solution case should be only about 2 cm.$^{-1}$, which is within the limit of error of our measurements and so cannot be detected. This is undoubtedly true also for the alkyl phenyl ketones (XLI–XLVIII) and *p*-xylyl alkyl ketones (XLIX–LVII) which show only the barest

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(23) W. J. Detroit and H. Hart, This Journal, **74**, 5215 (1952).

(24) R. T. Lagemann, R. Gwin, C. T. Lester, J. R. Proffitt and E. C. Suratt, *ibid.*, **73**, 3213 (1950).

(25) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Butterworth Scientific Publications, London, 1950, p. 169.

(26) R. A. Day, A. E. Robinson, J. M. Bellis and S. B. Till, This Journal, **72**, 1379 (1950).

(27) For any compound, a, Kirkwood has shown (see West and Edwards, *J. Chem. Phys.*, **5**, 14 (1937)) that if D is the dielectric constant of a solvent, $[\nu^{(a)}{}_{\text{Vapor}} - \nu^{(a)}{}_{\text{soln.}}]/\nu^{(a)}{}_{\text{Vapor}} = K(\text{a})(D - 1)/(2D + 1)$. For two compounds, a and b, of similar nature $K(\text{a}) = K(\text{b}) = K$, and it can be shown that $[\nu^{(a)}{}_{\text{soln.}} - \nu^{(b)}{}_{\text{soln.}}]/[\nu^{(a)}{}_{\text{Vapor}} - \nu^{(b)}{}_{\text{Vapor}}] = 1 - k(D - 1)/(2D + 1)$. Since $k(D - 1)/(2D + 1)$ is always positive the difference in solution frequencies will be less than that for the gaseous frequencies.

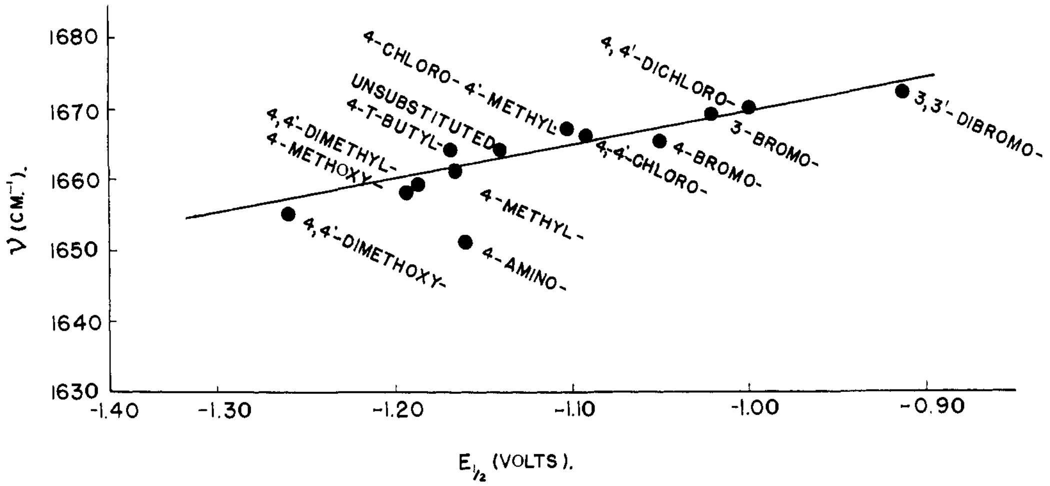

Fig. 2.—Carbonyl frequency *vs.* polarographic half-wave potential for substituted benzophenones in carbon tetrachloride solution.

of indications of ν(C=O) decreasing with increasing chain length.

When an alkyl side chain is branched at the carbon adjacent to the carbonyl carbon, the ν(C=O) drops, as is illustrated by following examples: $C{-}CO{-}C\langle^{C}_{C}$ (LX) (1718 cm.$^{-1}$), compared to C-CO-C-C-C (LXI) (1720 cm.$^{-1}$), and $^{C}_{C}\rangle C{-}CO{-}C\langle^{C}_{C}$ (LXIX) (1713 cm.$^{-1}$), compared to C-C-C-CO-C-C-C (LXVIII) (1716 cm.$^{-1}$). When the branching is not adjacent to the carbonyl carbon there is no effect upon the ν(C=O), *e.g.*, $C{-}CO{-}C{-}C\langle^{C}_{C}$ (LXII) (1720 cm.$^{-1}$). This "branching effect" is in correlation with the fact already observed that there is an increase of diamagnetism of branched hydrocarbons compared to normal isomers.[28]

H. **Epoxy Ketones.**—We have compared the carbonyl frequencies of 1,4-naphthoquinone-2,3-oxide (LXXV) and 1,4-naphthoquinone (LXXIV). Although the molecular rearrangement involved is complex, it should be noted that the elimination of the 2,3 conjugated double bond raises the frequency from 1675 to 1710 cm.$^{-1}$, as is evident from Table I. This frequency falls between that for aryl alkyl ketones, *ca.* 1692 cm.$^{-1}$, and for alkyl alkyl ketones, *ca.* 1719 cm.$^{-1}$.

We have also examined the effect upon the carbon tetrachloride solution frequency of the carbonyl group at position 20 of the epoxy group when fused to carbons 16 and 17 of the steroid skeleton's five-membered ring. In the two cases studied (LXXVII and LXXIX), as can be seen in Table I, the epoxy group has no effect upon the frequency of the neighboring carbonyl group.

Cromwell and Hudson have discussed the steric requirements for "three-ring carbonyl hyperconjugation."[29] Although these three-atom-ring containing compounds which we have studied (see also section A above for cyclopropane compounds) do not enable us to comment on this structural aspect of the problem, nevertheless we feel that in order to make a definitive analysis of the steric effect through infrared spectroscopy it is necessary to study compounds in a non-polar solvent. For example, Cromwell and Hudson have obtained solid state frequencies of 1677, 1670 and 1637 cm.$^{-1}$ for epoxy-perinaphthanone and perinaphthanone and perinaphthenone, respectively, in the course of their program to detect epoxy ring effects.[29] The carbon tetrachloride solution carbonyl frequencies of the latter two compounds are 1696 and 1646 cm.$^{-1}$, respectively.[13] The difference between solid and non-polar solvent frequencies is thus so great that it would be necessary to know the carbonyl frequency of epoxy-perinaphthanone in carbon tetrachloride solution in order to isolate the effect of the epoxy group upon the carbonyl frequency.

I. **Benzophenones.**—The polarographic oxidation–reduction potentials of fourteen substituted benzophenones have recently been measured by Brockman and Pearson.[30] We have measured the position of the carbonyl band for these substituted benzophenones (LXXX to XCIII) in carbon tetrachloride solution.[11] When these frequencies are plotted as a function of the corresponding polarographic half-wave potentials (Fig. 2), an approximately linear relationship is found. The slope of the ν(C=O) *vs.* $E^1/_2$ line in Fig. 2, 0.5 cm.$^{-1}$/centivolt, is of the same order of magnitude as the similar result for alkyl alkyl ketone series (Fig. 1) and for substituted quinones.[12,13]

Figure 3 is a graph of the same set of carbonyl frequencies as a function of the Hammett substituent constants, σ.[31] The uncertainty of ν(C=O) being ± 1 or ± 2 cm.$^{-1}$, and that of the σ averaging about ± 0.07,[31] it is clear that to a first approximation a linear relationship is found between ν(C=O) and σ.

The graph point for 4-aminobenzophenone (LXXXI) in Fig. 2 is the only one which has an $E_{1/2}$ value which is markedly below that which it should have in order to fall into position on the main se-

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[28] P. Pascal, A. Pacault and Hoaran, *Compt. rend.*, **233**, 1078 (1951).

[29] N. H. Cromwell and G. V. Hudson, THIS JOURNAL, **75**, 872 (1953).

[30] R. W. Brockman and D. E. Pearson, *ibid.*, **74**, 4128 (1952).

[31] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

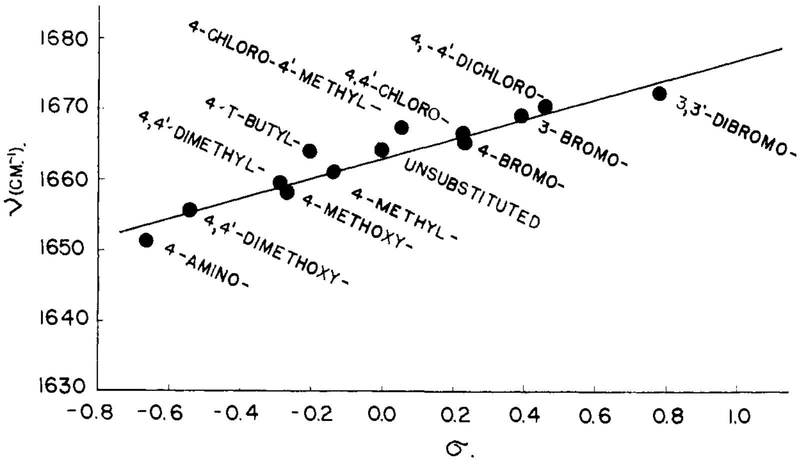

Fig. 3.—Carbonyl frequency *vs.* Hammett's substituent constant for substituted benzophenones in carbon tetrachloride solution.

quence. This 4-amino point also falls much below the main sequence of Brockman and Pearson's σ *vs.* $E_{1/2}$ graph.[30] These authors state that ". . . the amino group sigma value is not applicable under the conditions used (in obtaining the half-wave potential). In the acid buffer, the electron release ability of the basic amino group is undoubtedly diminished due to partial salt formation . . .". Our results in Fig. 2 bear out this conclusion. This is particularly evident when one observes that the 4-amino point does *not* behave anomalously in the σ *vs.* ν(C=O) plot (Fig. 3), a relationship in which the acid buffer condition does not take any part.

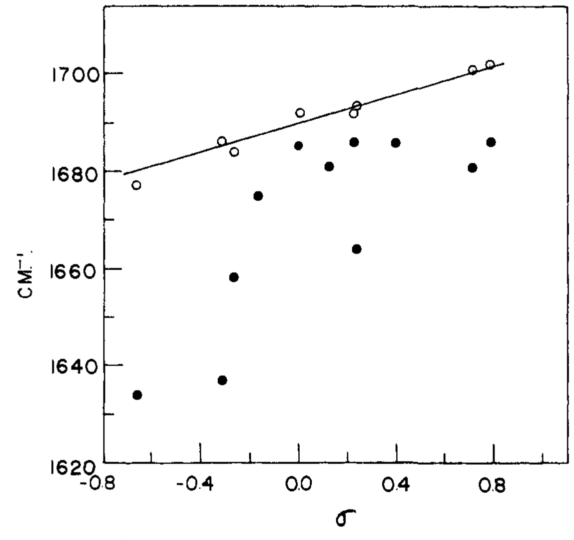

Fig. 4.—Carbonyl frequency *vs.* Hammett's substituent constant for substituted acetophenones in the natural solid (nujol mull) or liquid state, ●, and in carbon tetrachloride solution, ○. All natural state frequencies are taken from reference 32, with the exception of that for liquid acetophenone, which was obtained in this research. Three frequencies (those for *p*-methyl-, *m*-bromo- and *m*-methoxyacetophenone) were available only for samples in the natural state.

J. Acetophenones.—Soloway and Friess[32] were unable to find a simple relationship between ν(C=O) and σ for a series of substituted acetophenones. Their measurements being made in the solid state, we have repeated the study using dilute solutions in carbon tetrachloride. Figure 4 is a plot of ν(C=O) *vs.* σ for the solution frequencies given in Table I (XCIV–CI). Soloway and Friess's solid state frequencies[32] are plotted for comparison purposes. The contrast between the two underlines again the importance of working in dilute non-polar solution when comparisons of this kind are being sought.[12]

K. The Correlation between Hammett's Constants and the Carbonyl Frequency.—Flett in 1948 pointed out that if relations could be established between infrared frequencies and reaction rates, it would then be possible, in suitable cases, to use infrared frequencies to gain information about the electronic distribution in molecules for which rate data are not avail-

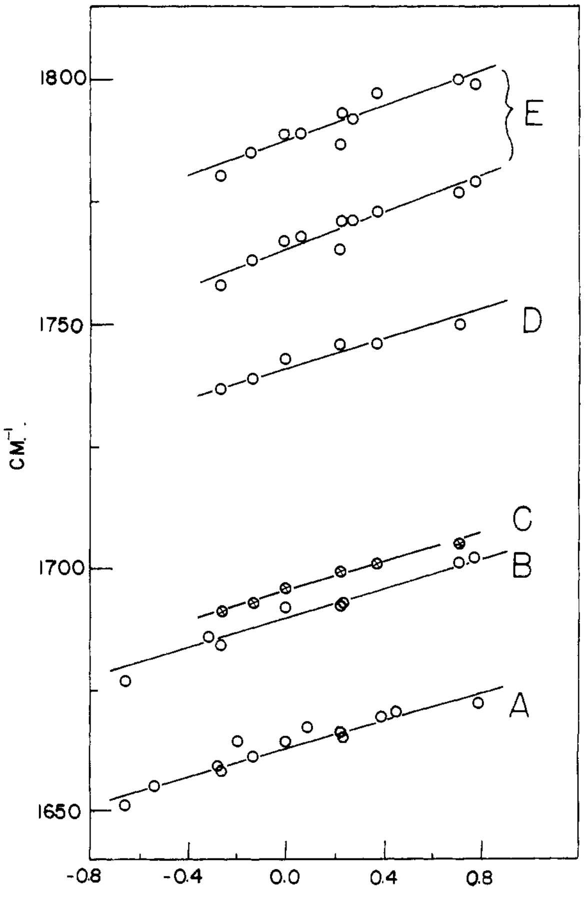

Fig. 5.—Carbonyl frequency *vs.* Hammett's substituent constant for substituted: (A) benzophenones; (B) acetophenones; (C) benzoic acid dimers; (D) benzoic acid monomers; and (E) symmetrical diacyl benzoyl peroxides . . . all in solution.

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(32) A. H. Soloway and S. L. Friess, This Journal, **73**, 5000 (1951).

able.[33] He illustrated this by the smooth relation he found between Hammett's constants and ν(C=O) for substituted benzoic acids. Davison[34] found a similar relationship to exist for substituted dibenzoyl peroxides and peresters.

The results we have obtained for substituted benzophenones and acetophenones add to the experimental data and enlarge the basis for the parallelism Davison found between his results and Flett's. Figure 5 summarizes the results obtained by Flett, Davison and ourselves. We have chosen to use a straight line as the functional relation best suited to express the results rather than to use curves such as Flett and Davison used. The ordinate and abscissa scales are chosen so that the uncertainty of the data is expressed by the size of the circular dots on the graph. The slope of the line for each set of data is almost the same, being about 15 cm.$^{-1}$ per sigma unit.

Jaffe has recently shown that σ is a monotonic function of electron density for *meta* and *para* substituted benzene ring compounds.[35] This adds importance to the infrared approach to measuring Hammett's constants.

Acknowledgment.—We should like to express our appreciation to Drs. Farber, Fieser, French, Hart, Iball, Julian, Lagemann, Mariella, Pearson and Soloway, who so generously supplied us with the compounds included in this study. We should like to thank Miss Jean-Marie Lebas, Miss Mary Edwards and Mr. David A. Danley for their help in obtaining some of the spectra. This investigation was supported by a Frederick Gardner Cottrell research grant from the Research Corporation.

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(33) M. St. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).

(34) W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951).

(35) H. H. Jaffe, *J. Chem. Phys.*, **20**, 279 (1952).

NASHVILLE, TENNESSEE

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY][1]

The Composition of Some Tetra-*t*-butyl Titanate–Glycol Reaction Products[2]

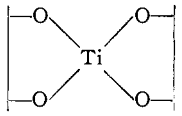
BY RICHARD E. REEVES AND LAURENCE W. MAZZENO, JR.

RECEIVED SEPTEMBER 28, 1953

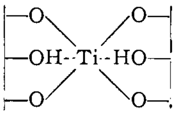
Accurate cryoscopic measurements can be made with tetra-*t*-butyl titanate (T*t*BT) in highly purified *t*-butyl alcohol. Such measurements on solutions of T*t*BT with ethylene glycol, octylene glycol or butanediol indicate the formation of molecular aggregates considerably larger than would occur if T*t*BT combined with one or two moles of glycol. Evidence is presented which strongly indicates the formation of a compound having the titanate : glycol ratio of 2:3; the species formed may actually contain 4 moles of titanate and 6 of glycol. The formation of other compounds having the compositions 2:2, 2:4 and 3:6 is also suggested. Thus it appears that T*t*BT does not form simple chelates with one or two bidentate glycol residues attached to a central titanium atom. On the other hand T*t*BT appears to react with ethyl acetoacetate to form 1:1 and 1:2 compounds. The present observations are discussed in relation to certain structural proposals which have appeared in the literature.

Tetraalkyl titanates are known to react with hydroxyl-containing polymeric substances such as cellulose acetate, cellulose nitrate and polyvinyl alcohol to produce insolubilization of the polymer. This effect has been attributed to titanium cross-linkages between the unsubstituted hydroxyl groups of two polymeric chains. Two structures which have been proposed to represent this interaction are shown below. Structure I, attributed by Schmidt[3] to Bayer and Nelles, involves a tetracoördinated titanium atom bound to two hydroxyl groups on each of two polymer chains; while II, proposed by Schmidt, involves hexa-coördinated titanium bound to three hydroxyl groups on each polymer chain.

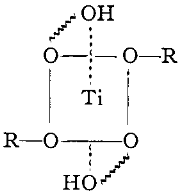
I



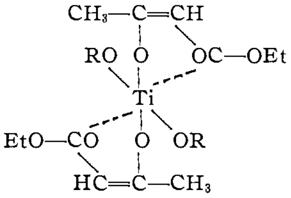
II



III



IV



Haslam[4] has studied the heats of reaction when tetraalkyl titanates react with certain bidentate groups and has attributed the large heats of reaction to the formation of stable chelate rings. It is known that the titanates undergo alcoholysis reactions with simple alcohols very readily, therefore it was reasonable to suppose that reaction with dihydroxy substances might produce chelate rings with a central titanium atom bound to one, two, or even three bidentate groups. Haslam found that most of the heat was evolved upon addition of two moles of bidentate ligand, hence he advanced structure III to represent his compounds. In this structure the wavy lines represent the hydrocarbon skeleton of a bidentate ligand such as octylene glycol. Schmidt[3] used a similar chelate structure, IV, to represent the product formed by the reaction of tetra-*n*-butyl titanate with two moles of ethyl acetoacetate.

It occurred to us that further information on the titanate–glycol and titanate–polymer structures might be obtained, advantageously, by means of

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[1] One of the laboratories of the Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] Presented at the Regional Conclave of the American Chemical Society, New Orleans, La., December, 1953.

[3] F. Schmidt, *Angew. Chem.*, **64**, 536 (1952).

[4] John H. Haslam, a manuscript entitled "Correlation of Properties of Titanium Esters with Structure" presented before the Division of Organic Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1952.