for *m*-di-*t*-butylbenzene, b.p. 101° (11.2 mm.), $n^{20}D$ 1.4879. The infrared spectrum was identical in every detail with the reported spectrum.[35]

Anal. Calcd. for $C_{14}H_{22}$: C, 88.33; H, 11.67. Found: C, 88.42; H, 11.66.

The residue consisted of 38 g. of brown, oily solid which, on washing with ethanol, yielded 36 g. of colorless crystals, m.p. 80–80.2° (crystallized twice from cyclohexane), b.p. 237°; a mixture melting point with authentic *p*-di-*t*-butylbenzene (Eastman Kodak Co.), m.p. 76.8–78°, b.p. 237°, showed no depression. In addition, the infrared spectra were identical.

The black solid left from steam distillation of the reaction mixture was dissolved in toluene, extracted with water, and evaporated to dryness yielding 26.5 g. of black, glassy solid.

Analytical Methods.—Analysis of the mixtures of chlorotoluene isomers was effected by use of a plot of the known concentration in cyclohexane solution *versus* the absorbance according to the base line method.[36] *Meta* isomer determinations were made by the differential method. The absorbance was measured at the indicated wave length (μ): *o*-chlorotoluene (13.40), *p*-chlorotoluene (12.45) and *m*-chlorotoluene (13.0). Comparison with known mixtures showed a deviation of no more than ±1% for the *p*-isomer. Infrared spectra were obtained with a Perkin–Elmer model 21 infrared spectrophotometer. Molecular weights were determined by the Rast method.

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[36] R. L. Bohon, R. Isaac, H. Hoftiezer and R. J. Zellner, *Anal. Chem.*, **30**, 245 (1958).

CLEVELAND, OHIO

[CONTRIBUTION FROM THE DOW CHEMICAL CO., WESTERN DIVISION]

Physical and Chemical Effects of Substituent Groups on Multiple Bonds. II. Thiolesters[1]

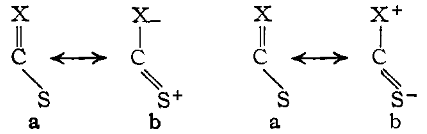
BY A. W. BAKER AND G. H. HARRIS

RECEIVED SEPTEMBER 11, 1959

Correlations of carbonyl frequencies and basicities have shown that sulfur in thiolesters participates in resonance interaction in the ground state through 3d-orbitals. The ν_{CO} values of thiolesters are 40–60 cm.$^{-1}$ lower than those of esters (almost the same as those of amides), but the carbonyl basicities are much lower. This precludes amide-type resonance.

The electronic structure of the chemical bonds in certain types of sulfur compounds has been unexpectedly variable and difficult to characterize. This is particularly evident in functional groups where sulfur can form multiple bonds to a single ligand, either by formal, non-charged structures or by conjugative interaction with an adjacent unsaturated group. While the former double bond structures have been the subject of many recent papers,[2-5] the latter have received relatively little attention and are not well understood.

One question of particular interest in compounds containing sulfur attached directly to a π-electron system pertains to the nature of the conjugative interaction and the type of orbitals used by sulfur in the consequent π-bond formation. Infrared spectra of vinyl sulfides or aliphatic and aromatic thiolesters show that the sulfur atom causes a surprisingly large perturbation on the adjacent double bond. For an ethylenic C=C group, this is much larger than the effect shown by oxygen and, for the carbonyl group, is in the opposite direction and nearly equivalent to the effect of nitrogen. It can be measured indirectly by the shift to lower frequencies of the characteristic double bond stretching vibrations, a shift which unquestionably is not due to mechanical coupling or physical mass effects. The cause of this perturbation has been described previously[6] as a reduction in the force constant of the double bond due to a conjugative shift of electrons away from the sulfur orbitals according to valence bond structures Ia and Ib. These involve the use of 3p-orbitals by sulfur.



a b a b

I II

However, it is now well known[7] that the 3p π-bonds of sulfur are much less stable than the 2p π-bonds of oxygen and that the electron release of divalent sulfur (–SR) is less than that of oxygen (–OR). It has also been shown conclusively that sulfur can expand its valence shell to 10 or more electrons under conditions which indicate that the energies required for d-orbital utilization are not exorbitantly high.[8] Therefore, despite the fact that atom X may have a higher electronegativity than sulfur, it is much more probable that the drift of electrons is in the opposite direction due to conjugative coupling of the type shown in structures IIa and IIb.

These two different types of resonance interaction, discussed below from the standpoint of orbital overlap, have opposite effects on the electron charge or bond hybridization of atom X. Consequently, when X is an atom having lone pair electrons (N,O), the availability or basicity of these electrons will be quite different according to the type of interaction. The conjugation shown in structure I will obviously increase the basicity of the lone pair electrons since the amount of p-character in these orbitals increases, but the conju-

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[1] Presented before an open scientific meeting June, 1958, at the Western Regional Research Laboratories, Bureau of Agriculture and Industrial Chemistry, Albany, Calif.

[2] (a) D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.*, 2442 (1949); (b) E. D. Amstutz, I. M. Hunsberger and J. J. Chessick, THIS JOURNAL, **73**, 1220 (1951).

[3] H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951).

[4] Hans Siebert, *Z. anorg. u. allgem. Chem.*, **275**, 210 (1954).

[5] W. Moffitt, *Proc. Roy. Soc.* (*London*), **200A**, 409 (1950).

[6] R. B. Barnes, R. C. Gore, V. Liddel and V. Z. Williams, "Infrared Spectroscopy," Reinhold Publishing Corp., New York, N. Y., 1944.

[7] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. II.

[8] D. P. Craig and E. A. Magnusson, *J. Chem. Soc.*, 4895 (1956).

gation in structure II will decrease the basicity for the opposite reason. Basicity measurements of appropriate carbonyl groups will, therefore, enable these two types of conjugation to be distinguished. We have used the hydrogen bonding method described by Cook[9] for this purpose and have found that in thiolesters the data support the type of interaction shown in structure II. Both $\nu_{C=O}$ and the carbonyl basicity decrease, whereas for amides in which only type I interaction can occur, $\nu_{C=O}$ decreases but the carbonyl basicity increases. Cook has well documented the claim that these measurements are indeed indices of electron availability or ease of electron removal and we feel that further proof is unnecessary here.

This paper will discuss these data with particular reference to thiolesters and their characteristic infrared frequencies. Additional confirmation for these suggestions is obtained from consideration of resonance integrals, π-electron contribution to dipole moments, and chemical reactivities of vinyl and acetylenic sulfides.

Experimental

The compounds examined in this paper were obtained from commercial sources when available or were prepared by conventional preparative procedures. For example, the preparation of several derivatives involved the reaction of CH_3SCOCl with the appropriate -NH, -OH or -SH compounds with subsequent distillation purification. The commercial samples generally were run as received, but several were distilled and re-examined; no change was observed in the spectral data.

The infrared spectra were obtained with a Beckman IR-7 prism-grating spectrophotometer using a slit program which gave a resolution of about 1.0 cm.$^{-1}$. The carbonyl frequencies were measured in CCl_4 at concentrations of 2 and 0.02% in cells 0.1 and 10 mm., respectively. No appreciable change on dilution was observed for any compound. The relative basicities of each of the carbonyl groups were established by the strength of the hydrogen bond between the oxygen and the acetylenic C-H group of phenylacetylene. This last compound was dissolved 0.5-2.0% weight per volume in each sample and the acetylenic C-H frequency measured. The lower concentration limit was found to be essential for those compounds of low carbonyl basicity in order to eliminate interfering side effects and self association of phenylacetylene. Frequencies of the C-H group could be measured to better than ± 0.5 cm.$^{-1}$ except for a few instances in which the bands were broad and the minimum poorly defined. Where the compound also had been run by Cook, the agreement between data generally was satisfactory. However, we feel that our data are more accurate due to the higher performance of the Beckman spectrophotometer.

Results

The acetylenic C-H group of phenylacetylene can, as shown by Cook,[9] interact with an electron donor group to form a weak complex or hydrogen bonded pair. The interaction lowers the C-H stretching frequencies by an amount dependent upon the basicity of the donor atom. In agreement with the observations of Bellamy[10] on other types of intermolecular associations, this is primarily a specific type of molecule-molecule interaction and is less influenced by the dielectric strength of the solution. This is shown by the complex structure of the C-H band in solvents containing more than one donor group and by the occurrence of two bands of varying intensities in chlorinated solvents where there is only one kind of basic group. In this latter class of compounds, the doubling of the C-H bands may be due in part to the presence of free and bonded C-H groups but it may also be due to Fermi interaction between the C-H stretching fundamental and the second overtone of the C-H deformation mode. This doubling is a sensitive function of of the solvent as shown by the data of Table I which give the frequencies of these two bands in typical chlorocarbons and the "free/bonded" absorbance ratios. This effect is also temperature sensitive as shown by heating a solution of phenylacetylene in hexachlorobutadiene. At 70°, the "associated" band had nearly disappeared and at 100° it had disappeared altogether.

TABLE I

Compound	Free	Bonded	Absorbance ratio
Perfluorodimethylcyclohexane	3331.3	....	
CCl_4	3315.7	3305.0	1.37
$Cl_2C{=}CClClC{=}CCl_2$	3313.2	3303.7	1.16
CH_2Cl_2	3308.8	3297.2	0.97

TABLE II

FREQUENCY CORRELATIONS OF CARBONYL COMPOUNDS

	Compound[aa]	ν_{CO}	ν_{CH}(assoc.)	ν_{CH}(unassoc.)
1	CH_3COCl	1806.9	3295.1	3308.8
2	CH_3OCOCl	1787.0	3294.8	3309.2
3	$CH_3COOC_6H_5$	1767.6	3281.4	3303.3
4	CH_3SCOCl^a	1766.0	3294.8	3308.1
5	$C_2H_5OCOOC_6H_5{}^b$	1764.2	3286.7	3304.1
6	$CH_2{=}CHCOCl$	1761.6	3294.0	3308.5
7	$CH_3OCOOCH_3$	1757.4	3278.9	3304.5
8	CH_3COOCH_3	1748.8	3266.8	3304.5
8a	$(CH_3)_2NCOCl$	1744.8	3265.0	3304.1
9	$CH_2{=}CHCOOCH_3$	1734.1	3268.0	3305.5
10	$CH_3SCOOC_6H_5{}^c$	1733.9	3288.4	
11	$HCOOC_2H_5$	1731.0	3275.6	3305.5
12	$C_6H_5COOCH_3$	1729.0	3265.0	3305.5
13	$CH_2{=}C(CH_3)COOCH_3$	1726.5	3266.5	3305.3
14	$CH_3OCOSCH_3{}^d$	1718.8	3286.6	3304.1
15	$CH_3COCH(CH_3)_2$	1718.6	3257.6	
16	CH_3COCH_3	1718.0	3257.3	3301.6
17	$CH_3COSC_6H_5{}^e$	1713.6	3283.2	3303.3
18	$CH_3COSCH_3{}^f$	1698.1	3273.8	3304.1
19	$C_6H_5COCH_3$	1691.6	3260.0	3303.5
20	$HCON(CH_3)_2$	1687.4	3221.1	
21	$CH_2{=}CHCOCH_3$	1686.3	3259.6	
22	$C_5H_5COSC_2H_5{}^g$	1668.6	3271.4	
23	$(CH_3)_2NCOSCH_3{}^h$	1661.6	3238.5	
24	$(CH_3)_2NCON(CH_3)_2{}^i$	1654.4	3210.3	
25	$CH_3SCOSCH_3{}^j$	1653.0	3288.8	3303.5

[aa] The compounds with alphabetical references were prepared here and have the boiling points: [a] 110°, [b] 103-104° (11.5 mm.), [c] 109° (1 mm.), [d] 120-121, [e] 98-105° (4 mm.), [f] 99-100°, [g] 134° (20 mm.), [h] 176°, [i] 83° (22 mm.), [j] 169°.

In the carbonyl compounds examined, the intensity of the free C-H band varies from a slight shoulder in strongly basic compounds such as dimethylformamide to about 80% of the intensity of the associated band in compounds such as acetyl chloride. In those compounds containing an aromatic ring, there is another band near 3290

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(9) D. Cook, THIS JOURNAL, **80**, 49 (1958).

(10) L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959).

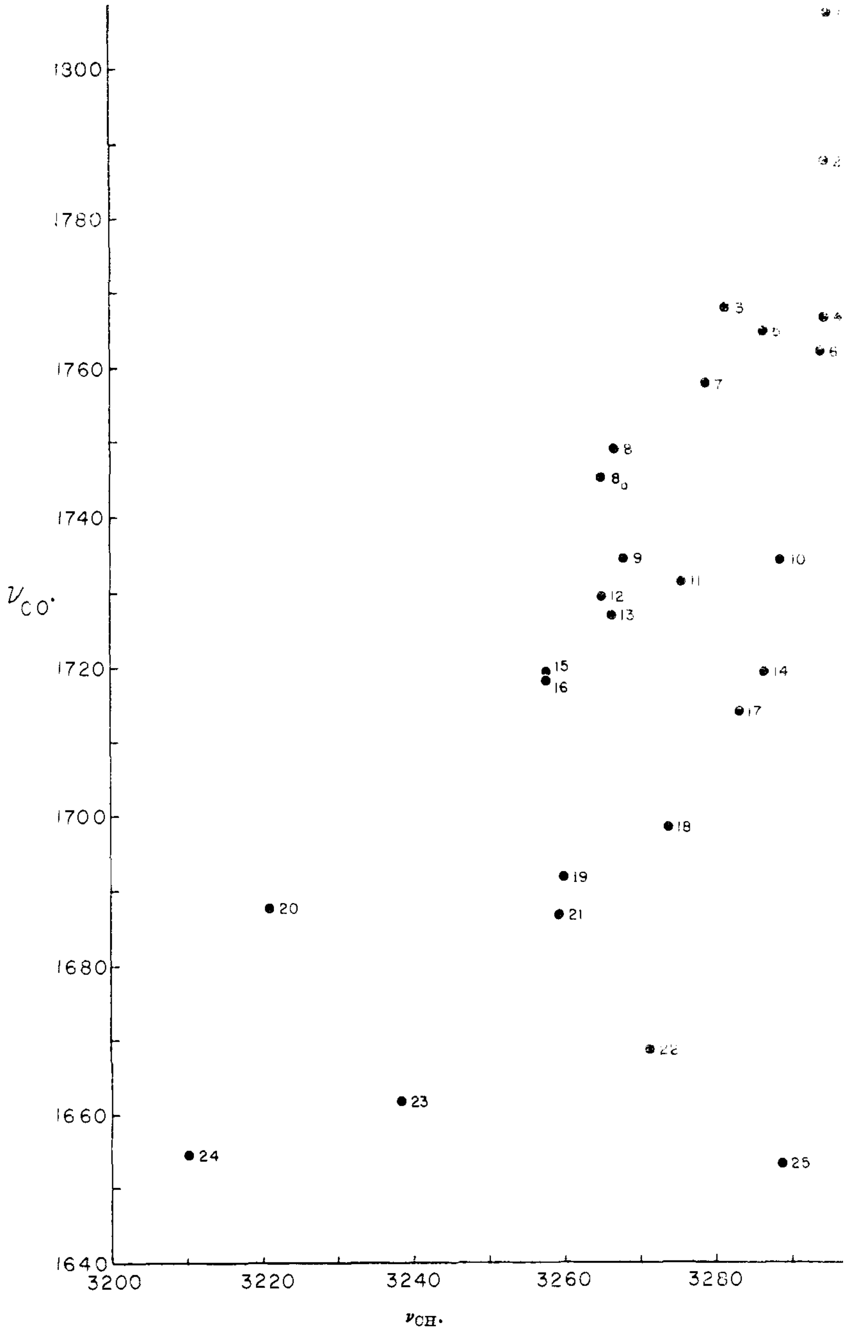

Fig. 1.—Plot of carbonyl frequencies against phenylacetylene C–H frequencies. The carbonyl frequencies were obtained from dilute solutions in CCl_4; the C–H frequencies were obtained by dissolving phenylacetylene in the appropriate carbonyl compound.

cm.$^{-1}$ due to interaction with the aromatic π-electrons (3293.3 cm.$^{-1}$ for benzene). This band overlaps the third band due to bonding to the carbonyl oxygen in those compounds in which the basicity of the oxygen is low, but in some compounds, such as methyl benzoate, the three are all clearly resolved. This overlapping of bands in the majority of aromatic compounds makes the exact frequencies difficult to measure. There is indication that a similar problem also occurs in vinyl compounds.

The free and bonded acetylenic frequencies are listed in Table II, together with the carbonyl frequencies of the corresponding compounds. Figure 1 shows the values of ν_{CH}, plotted against the values of ν_{CO}. Cook was able to show a general tendency for the conjugated and unconjugated compounds to fall on two lines of different slope. However, he dealt with a fairly limited class of compounds in which the structural groups were all quite similar. When a greater variety of samples are compared, including various combinations of oxygen, nitrogen, sulfur, chlorine and π-electron systems adjacent to the carbonyl group, no such correlations can be observed, probably because of the complex nature of the interactions. However, Cook's data and those given in Fig. 1 indicate that the following conclusions can be made as general statements for all of the compounds listed: (1) the basicities of the carbonyl oxygen in ethylenic and aromatic ketones are generally lower than those of normal aliphatic ketones. This is contrary to the general assumption concerning the importance of dipolar valence bond structures wherein oxygen has a negative charge, and indicates that the polarizing effect of a carbonyl group for a neighboring π-electron system is very much lower than commonly believed.

(2) Sulfur and chlorine in thiolesters and acyl chlorides, compared to aliphatic ketones, both reduce carbonyl basicity (by resonance and induction, respectively) but have opposite and very pronounced effects on ν_{CO}. Since the electronegativity of sulfur is only slightly greater than that of carbon, the only apparent way sulfur could cause a large decrease in both basicity and carbonyl frequency is by a π-electron withdrawal from the C=O bond. This is consistent with the comparatively large increase in the frequency of the sulfur–carbon vibration from the normal 600–700 cm.$^{-1}$ C–S single bond range to 850–1000 cm.$^{-1}$ in thiolesters.

(3) Nitrogen and sulfur in amides and thiolesters both cause large reductions in carbonyl frequency but influence the carbonyl basicity in opposite ways. Since the π-orbital overlap in amides can only occur by donation of the lone pair nitrogen

electrons, the carbonyl oxygen gains a net electronic charge and becomes more basic. Similar effects should be observed in thiolesters if the same type of π-orbital overlap occurred.

The substitution of two sulfur atoms onto the carbonyl group, as in dithiolcarbonates, causes a further large decrease in frequency and a small additional decrease in basicity. It is probable that the decrease in basicity measured by these techniques is asymptotically limited by the ν_{CH} values of the unassociated C–H groups and influenced by the increasing importance of second-order interactions as the extent of bonding decreases. In this respect, it is interesting to note that the $\Delta\nu_{CH}$ values (the difference between the two C–H frequencies in each compound) vary only slightly for compounds in which the value of ν_{CH} for the associated C–H is greater than about 3287 cm.$^{-1}$.

On the other hand, two disubstituted nitrogen groups, as in tetramethylurea, cause relatively little additional change in either basicity or carbonyl frequency than that produced by a single nitrogen. This probably can be ascribed to the fact that such a molecule cannot be coplanar because of steric interactions between the substituents on the two nitrogen atoms. Therefore, only one nitrogen at a time can have full π-orbital overlap with the carbonyl group. As a secondary effect, this interaction between the two substituted nitrogen groups possibly tends to open out the N–C–N angle to greater than 120° and thereby to change hybridization of the carbon orbitals. In analogy with Lord and Miller's discussion[11] of the effects which ring size of cyclic ketones has on the carbonyl frequency, this change would decrease the carbonyl frequency but would possibly influence the carbonyl basicity only indirectly. Consequently, such compounds would not necessarily fall directly on the curve for conjugated carbonyl groups. A similar decrease in ν_{CO} due to steric interaction is probably shown by disubstituted amides. For example, the carbonyl frequency of N,N-dimethylacetamide (1662 cm.$^{-1}$) is 27 cm.$^{-1}$ lower than that of N-methylacetamide (1689 cm.$^{-1}$).

(4) Mixed groups, as one would expect, tend to fall between the values for carbonyl groups disubstituted with either group alone. This is shown by the two series $CH_3OCOOCH_3$, $CH_3SCOOCH_3$ and $CH_3SCOSCH_3$; and CH_3COCH_3, CH_3SCOCH_3 and $CH_3SCOSCH_3$. Except for the interfering steric interactions in tetramethylurea, the same trend is shown by $(CH_3)_2NCON(CH_3)_2$, $(CH_3)_2NCOSCH_3$ and $CH_3SCOSCH_3$.

Discussion

Polar Effects.—Aside from steric effects or group associations, the values of ν_{CO} are altered primarily by differences in the inductive and resonance properties of the substituent groups. Increasing the inductive effect (by increasing the electronegativity of the substituent groups) increases ν_{CO}[11] but very markedly decreases carbonyl basicity. On the other hand, increasing the resonance interaction, or π-orbital overlap, decreases ν_{CO} but it can either increase or decrease carbonyl basicity depending upon the type of interacting orbitals. Inasmuch as electronegativity is generally proportional to inductive capacity, oxygen is expected to have a larger effect than chlorine due to its greater electronegativity. However, the data of Table I show that in all cases where chlorine is replaced by an OR group, ν_{CO} decreases and carbonyl basicity increases. Therefore, contrary to the conclusions of Cook who noted that the ν_{CH}–ν_{CO} correlations were typical of saturated compounds, we conclude that oxygen has a very pronounced resonance effect which is not evident from relationships of this kind because of compensating interactions. This conclusion is supported by the resonance contributions of Hammett sigma parameters listed by Taft.[12] He gives a value of $+0.25$ for a CH_3CO group and a value of -0.50 for a CH_3O group. Inasmuch as the former is a moderately strong electron acceptor and the latter a very strong donor, it would be extremely unusual for these two groups not to show some type of resonance interaction when their interactions with a phenyl ring are so large. Moreover, it is important to note that even if the bonds of the ester group in an aliphatic ester are not strictly coplanar, π-orbital overlap can still be approximately 50% of the full coplanar value for a rotation of 45°.[13] Further, the donor properties of CH_3O also are evident in comparison of ν_{CO} values for CH_3COCl and CH_3OCOCl. The carbonyl frequency of the latter compound is 19.9 cm.$^{-1}$ lower than that of the former and the carbonyl basicity is slightly larger possibly because the electron withdrawal by the chlorine makes the resonance effect of the CH_3O group larger than the inductive effect.

Characteristic Frequencies of the Thiolester Group.—In addition to the fact that the carbonyl frequency of thiolesters is 40–60 cm.$^{-1}$ lower than that of normal esters, the S–C stretching frequency is very markedly increased over the values found in saturated aliphatic sulfides. Sheppard[14] has found that in sulfides the S–C characteristic frequency occurs in the range 600–700 cm.$^{-1}$ and he has noted its weak intensity in some compounds. Mecke, *et al.*,[15] observed that the S–C frequency in thiolesters increases to 800–900 cm.$^{-1}$, whereas we extend the range to 1000 cm.$^{-1}$ or slightly more for compounds of the type $RSCOCH_2Cl$. The intensity of this band varies over rather extreme values from a weak band in methyl thiolacetate to the strongest and broadest band in the spectra of compounds such as RSCOCl. The increase of this characteristic frequency is indicative of a strong resonance effect but in itself does not distinguish between the two types discussed above.

Evidence for Weakness of 3p π-Orbital Overlap.—It has long been noted from chemical evidence that the ability of sulfur to donate or share electrons (through 3p π-orbital overlap) is much less than that of oxygen. Thus the electron donating (+M effect) of a sulfide sulfur is less than that of an

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[11] R. C. Lord and F. A. Miller, *Appl. Spectroscopy*, **10**, 115 (1956).

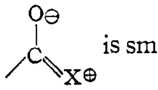
[12] R. W. Taft, Jr., This Journal, **79**, 1045 (1957).

[13] L. L. Ingraham, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 483.

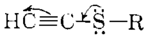
[14] N. Sheppard, *Trans. Faraday Soc.*, **46**, 429 (1950).

[15] Rolf Mecke, Reinhard Mecke and A. Luttringhaus, *Chem. Ber.*, **90**, 975 (1957).

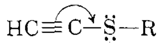
ether oxygen and the electron-attracting power (-I effect) of a thiocarbonyl group is greater than that of a carbonyl group.[7] These observations are supported by the values of overlap integrals calculated by Robertson and Matsen.[16] Following the suggestion of Mulliken[17] that the overlap integrals vary in the same way as do the resonance integrals, these authors have shown that resonance interaction decreases along the series C > N > O > S.

Despite the fact that S_{CS} is greater than S_{CO}, they have shown from ultraviolet spectra that β_{CS} (the resonance integral of carbon and sulfur) is less than β_{CO}, a conclusion previously suggested by Wheland and Pauling.[18] Therefore, it is reasonably certain that resonance interaction involving only 3p-sulfur orbitals is quite small. This is further confirmed by recent chemical data[19] showing that the resonance interaction  is smaller in thiolesters than in esters.

Prior Evidence for 3d π-Orbital Overlap.—On the other hand, the ability of sulfur to expand its valence shell to 10 or more electrons in covalent bonds has been well substantiated. These ideas have been extended in a few instances to the concepts of conjugation, although in most cases d-orbital utilization is postulated only for excited or intermediate states. Recently Volger and Arens[20] compared the addition reactions of ethoxyethyne with those of ethylthioethyne and concluded that sulfur displayed the dual nature of being able to increase its covalency either by $C_{2p}\pi$–$S_{3p}\pi$-orbital overlap (structure III) or by $C_{2p}\pi$–$S_{3d}\pi$ orbital overlap (structure IV).



III



IV

In regard to structure III, however, both their data and the data they quote[21] concerning the effect on benzoic acidity of *para* $-OCH_3$ and $-SCH_3$ groups indicate that this type of resonance occurs only to a very slight extent and then only under extreme conditions of electron withdrawal. The type indicated by structure IV was shown to occur quite readily but they concluded that both effects were due primarily to polarization induced by the attacking species and that the electron shift was created only as the attacking group approached the reactive center.

Additional chemical support for 10-electron sulfur in resonance was given by earlier observations[22–23] that the sulfur atom in sulfides has a greater acidifying effect on the α-hydrogen atoms than does the oxygen atom in ethers. This is contrary to the order expected from the difference in electronegativities, and suggests that forms such as $—C{=}\bar{S}—$ stabilize the anion after proton release. In a similar way, the mechanism of the isomerization of alkylaryl sulfides is believed to involve the removal of a proton to form an anion that is stabilized by 10-electron sulfur.[24] Physical evidence for the resonance participation of the 3d-orbitals of sulfur has appeared recently for four types of sulfur compounds.[25–28] In the former two, ultraviolet spectra were interpreted as indicating that 3d-orbitals were involved in the excited state of aromatic thiolesters and *o*-hydroxyphenyl sulfides. The interaction in the thiolesters was considered to be primarily between the aromatic ring and the sulfur and not between the sulfur and the carbonyl group. In the latter two types of compounds, dipole moments (of aromatic sulfones) and resonance energies (of thiophene compounds) were held to be indicative of ground state participation of the sulfur d-orbitals. This gives ample support for the above suggestion that the 3d-orbitals of sulfur can participate in resonance interaction in the ground state without a special or extreme amount of stabilizing energy. Moreover, as judged by the effects on the carbonyl group, the resonance is comparatively large in thiolesters despite the fact that oxygen is expected to polarize the π-cloud away from the carbon atom. However, recent calculations by Brown[29] indicate that the π-cloud polarization is much less than has been previously believed and that most of the carbonyl dipole moment is due, not to polarization effects, but to the lone-pair hybrid orbitals on the oxygen atom. Therefore, the fact that the carbonyl group can lose charge to the sulfur atom is not too surprising.

The unusually large value of the sulfur–carbon interaction in thiophene has been adequately explained by Longuet-Higgins[28] as being due to a pd-hybridization of the sulfur orbitals. Such rehybridization of the sulfur orbitals would explain the large resonance interaction in thiolesters because the overlap integrals would become markedly larger upon inclusion of the d-orbitals. It is reasonable to extend this concept to all compounds in which sulfur is attached directly to an unsaturated group or to a group having available molecular orbitals for resonance interaction. This suggestion has been made[30] even for the S_8 sulfur ring or linear chain in which each of the bonds is believed to be a partial double bond.

Classification of Resonance Mechanisms.—In view of the above data, we conclude that resonance interaction can be generalized into three different categories depending upon the types of orbitals used to establish the resultant molecular orbitals:

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(16) W. W. Robertson and F. A. Matsen, THIS JOURNAL, **72**, 5248 (1950).

(17) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

(18) G. W. Wheland and L. Pauling, THIS JOURNAL, **57**, 2086 (1935).

(19) M. W. Cronyn, M. P. Chang and R. A. Wall, *ibid.*, **77**, 3031 (1955).

(20) H. C. Volger and J. F. Arens, *Rec. trav. chim.*, **77**, 1170 (1958).

(21) F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **74**, 1058 (1952).

(22) R. B. Woodward and R. H. Eastman, *ibid.*, **68**, 2229 (1946).

(23) W. J. Brehm and T. Levenson, *ibid.*, **76**, 5389 (1954).

(24) D. S. Tarbell and M. A. McCall, *ibid.*, **74**, 48 (1952); D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956).

(25) G. Cilento, *Experientia*, **8**, 421 (1952); THIS JOURNAL, **75**, 3748 (1953); *J. Org. Chem.*, **24**, 413 (1959).

(26) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 84, 2889 (1949).

(27) M. T. Rogers, G. M. Barrow and F. G. Bordwell, *ibid.*, **78**, 1790 (1956).

(28) H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **45**, 173 (1949).

(29) R. D. Brown and M. L. Heffernan, *ibid.*, **54**, 757 (1958).

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(1) One category comprises the interaction between two π-bond systems as in butadiene or vinyl ketones. Here, the π-orbitals overlap the center C–C single bond and increase its charge density and bond strength. In consequence, both of the adjacent double bonds (or unsaturated groups) lose charge and the bond strengths (and basicities of carbonyl groups) decrease. For conjugated carbonyl compounds, as the polarizability of the adjacent group increases the π-orbital overlap increases and the oxygen basicity also increases due to a greater release of charge to the carbonyl group (or possibly less charge is withdrawn from the carbonyl group since even acetophenone and methyl vinyl ketone are less basic than acetone).

(2) Conjugation, as in amides where an electron-donating atom is attached to a π-electron system: If no unoccupied orbitals are energetically available on this atom, then the only type of π-orbital overlap which can occur is by the donation of the lone pair of electrons into a molecular orbital extending over the donating atom and the adjacent unsaturated group. The force constants of the N—C bond and the C=O bond increase as did the central C—C bond in conjugated ketones, but the carbonyl basicity increases.

(3) Conjugation, as in thiolesters, where an electron-receiving atom is attached to a π-electron system: In this case, the group molecular orbital is set up by a $p\pi$–$d\pi$-orbital overlap allowing a certain amount of electron drift from the carbonyl bond into the sulfur orbitals thus decreasing the force constant of C=O, but increasing that of C—S. This markedly lowers the carbonyl basicity but not as effectively as does a single halogen.

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The Introduction of *n*-Alkyl Groups into Phenols and Hydroquinones

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Acylation of *n*-alkylhydroquinones and *n*- and *sec*-alkylphenols proceeds in the presence of boron trifluoride without isomerization of the alkyl groups. Reduction of the carbonyl groups (or of their Grignard reaction products) furnishes di- and tri- *n*- (or *sec*-)alkyl products.

Dialkylphenols[1] and dialkylhydroquinones[2–4] with alkyl groups of 3 to 18 carbon atoms are used in color photography. Properties such as melting point, solubility, diffusivity and resistance to aerial oxidation of the side chains vary with the nature of the side chains, and *n*-alkyl derivatives could be expected to offer advantages.

While the number of known alkylphenols and alkylhydroquinones is considerable, few authentic derivatives with two (or more) *n*-alkyl groups have been prepared. Direct alkylation has resulted in mixtures of isomers which differ in the location of the aliphatic chain on the ring and in the structure of the chain itself.[5] Acylation in the presence of catalysts such as aluminum chloride[5,6] (Friedel–Crafts, Fries), followed by reduction of the ketones, yields mono-*n*-alkylphenols[7] and mono-*n*-alkylhydroquinone dialkyl ethers.[8–12] Cruickshank and Robinson[8] have prepared 2-*n*-amyl-5-*n*-octylhydroquinone by such reactions; the yield and difficulties in isolation and characterization of the product discouraged us from using a similar route for the preparation of larger amounts. Moreover, it was verified that acylation of 4-*n*-alkylphenols and of their ethers with aluminum chloride catalyst results in extensive isomerization of the *n*-alkyl groups. For example, 4-*t*-amylphenol was isolated from a reaction involving 4-*n*-amylphenol, and mass spectrographic examination revealed isomerization of the amyl group of 4-*n*-amylanisole during an acylation reaction with $AlCl_3$ at 0°.

The desired di-*n*-alkyl compounds become readily available when boron trifluoride is used as an acylation catalyst[13,14]; ring acylations by aliphatic acids proceed without isomerization of normal chains in the starting materials and reduction yields di-*n*-alkylphenols and hydroquinones, respectively. A variety of di- and tri-*n*-alkylphenols has been made with smooth reactions. The mildness of the catalyst has also permitted acylation of *sec*-alkylphenols, without isomerization.

The synthesis of hydroquinone derivatives was

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