TABLE IV

RATE DATA FOR OXIDATION OF VI AND VII WITH ACETYL PEROXIDE IN ACETONITRILE AT 30°

	Initial concentrations			
Amine	[Peroxide] $\times 10^{-2}$	[Amine] $\times 10^{-4}$	$k' \times 10^4$ sec^{-1}	Standard deviation
VI	2.48	1.57	0.220	0.008
	2.48	1.57	0.217	0.012
	2.48	1.57	0.218	0.012
VII	2.48	1.52	0.208	0.014
	2.48	1.52	0.214	0.017
	2.48	1.52	0.209	0.016

VIII probably does not involve breaking of the nitrogen–hydrogen bond in the transition state of the reaction and may likely be an electron-transfer process.

Experimental Section

Materials.—*tert*-Butyl peroxide (Wallace and Tiernan, Inc.) and a 25% solution of acetyl peroxide in dimethyl phthalate (Wallace and Tiernan, Inc.) were used without further purification. *tert*-Butyl peracetate (Wallace and Tiernan, Inc.) (75% perester in benzene) was purified by vacuum distillation. The following commercial reagents were distilled twice before using: 2-butanol (from sodium), tetrahydrofuran (from sodium), and acetonitrile (from phosphorous pentoxide).

3,5-Dicarbethoxy-1,4-dihydro-2,6-lutidine (VI) was prepared from acetoacetic ester, formaldehyde, and ammonia by the method of Singer and McElvain[9] (mp 183–185°).

1-Deuterio-3,5-dicarbethoxy-1,4-dihydro-2,6-lutidine (VII) was prepared by allowing a mixture of 5 g of VI to reflux for 2 hr with 10 ml of deuterium oxide in 100 ml of dimethoxyethane. The compound was isolated and recrystallized from ethanol and the process repeated twice with fresh deuterium oxide. After the final exchange, no nitrogen–hydrogen bond could be observed in either the infrared or the nmr spectra of the material.

O-d-2-**Butanol** (V) was prepared by reaction of the sodium alkoxide with deuterium oxide in the following manner. Freshly distilled 2-butanol (500 ml) and sodium (20 g) cut in small pieces were placed in a 1-l. round-bottomed flask equipped with a reflux condenser. After the initial rapid reaction the mixture was heated at reflux for an additional 16 hr during which period all of the sodium reacted. Excess 2-butanol was removed under a vacuum leaving a white solid which was heated under vacuum for an additional 24 hr. Deuterium oxide (20 ml) was added to the dry solid producing a reddish brown mixture. The organic layer was distilled twice yielding *O-d*-2-butanol that by nmr analysis was 99% deuterated (30.2 g, 47% theory).

Peroxide Decomposition Rates.—The rates of reaction of *tert*-butyl peroxide in 2-butanol and *O*-D-2-butanol were determined by the gas chromatographic method described previously.[3] The decomposition rate of *tert*-butyl peroxide in the tetrahydrofuran solutions of VI and VII were also made by the gas chromatographic analysis of the unreacted peroxide as previously described.[4]

The decomposition rates of acetyl peroxide and *tert*-butyl peracetate in the presence of 2-butanol and *O-d*-2-butanol were determined by the method described by Silbert and Swern;[10] 1-ml samples of the reaction mixture were pipeted into a flask through which nitrogen had been passed for 20 sec. A saturated sodium iodide solution (about 2 ml) and 15 ml of freshly distilled glacial acetic acid containing 0.002% ferric chloride were added to the contents in the flask. The flask was stoppered and permitted to stand in the dark for 10–15 min. About 50 ml of distilled water was added to the solution which was titrated to a starch–iodine end point with 0.2 *N* thiosulfate to determine the amount of molecular iodine produced. A blank determination was run on all of the reagents.

Spectrophotometric Determination of Oxidation of Dihydrolutidines with Acetyl Peroxide.—Stock solutions of VI and VII in acetonitrile and of the acetyl peroxide–dimethyl phthalate solution in the same solvent were prepared. Samples of these solutions were thermostated at 30° before mixing. Immediately after mixing, the solutions were placed in a thermostatically controlled cell compartment of a Beckman DU spectrophotometer. The rates of reaction of the dihydropyridine derivatives were followed by measuring their absorption at 363 mμ as a function of time.

Registry No.—I, 110-05-4; II, 110-22-5; III, 107-71-1; 2-butanol, 78-92-2; V, 4712-39-4; VI, 1149-23-1; VII, 25894-44-4.

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(9) A. Singer and S. M. McElvain, "Organic Syntheses," Coll. Vol. II, Wiley, New York, N. Y., 1943, p 214.

(10) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

Substituent Effects in Alkali Metal–Ketyl Ion Pairs. An Infrared Scrutiny

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The carbonyl stretching frequency (ir) of alkali metal-4,4′-disubstituted ketyl ion pairs shows a startling deviation from the expected influence of five para substituents. Measurements indicate that the ketyl C–O bond is strengthened, rather than loosened, by electron-donating substituents. Plots of $\sigma_R{}^+$ *vs.* ketyl frequency are given. A possible explanation lies in the consideration of ion pairing by the counterion M^+ with increased electron density at the ketyl site. Such ion pairing might be able to reduce the antibonding influence of the added electron, thus allowing bonding π electrons to exert a stronger bonding force between the carbon and the oxygen atoms.

The utility of the carbon–oxygen stretching frequency of ketones as a sensitive indicator of electron density changes has long been recognized. Shifts in the carbonyl frequency are subject to both inductive and mesomeric effects which change the electron density at the carbon–oxygen bond.[2] Correlation of Hammett σ values with the carbonyl stretching frequencies in five 4,4′-disubstituted benzophenones has been shown to be nearly linear.[3] In essence, the studies all show that the greater the electron density at the C═O site, the lower the frequency (in cm^{-1}).

A one-electron reduction of a ketone results in a ketyl with the commonly given valence bond structure of $\dot{>}C{-}\bar{O}$. Such a structure does not reflect the fact that only one of the π electrons of the C═O bond has been essentially "cancelled" by the introduction of the new electron into the lowest antibonding orbital of the

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(2) (a) R. E. Kagarise, *J. Amer. Chem. Soc.*, **77**, 1377 (1955); (b) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 241 ff.

(3) N. Fuson, M.-L. Jósien, and E. M. Shelton, *J. Amer. Chem. Soc.*, **76**, 2526 (1954).

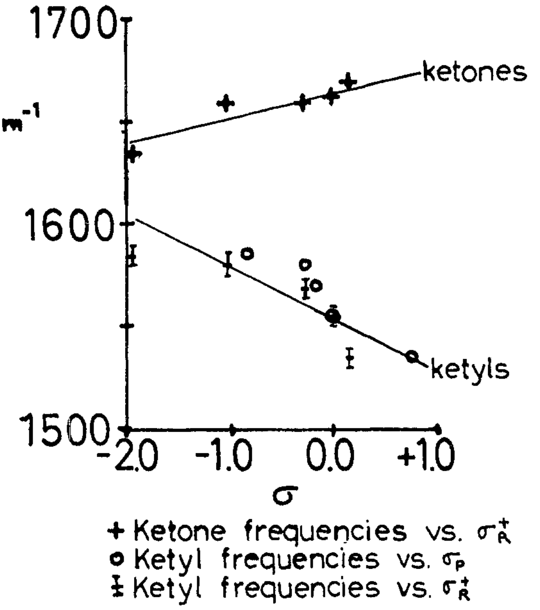

Figure 1.

carbonyl system. Thus the actual result is the "loosening" of the C═O stretching frequency by an amount equivalent to one-half of a π bond. Only a two-electron reduction would result in frequencies which might be considered to be comparable to C–O (zero π-bond order) stretching frequencies. The attachment of an aromatic group to the ketyl (*e.g.*, benzophenone anion radical) results in the delocalization of the odd electron from the ketyl group, significantly reducing the effect of the added electron upon the carbonyl stretching frequency.[4] For instance, the electron density of benzophenone as studied by epr results in a total electron density on the carbonyl ketyl of only 0.415.[5]

Experimental Section

Previous work definitely indicates the feasibility of producing anion radicals for study by infrared spectroscopy, and some measurements have been made on the frequency shifts of several types of aromatic compounds.[4,6] We realize that stretching frequency is not an absolute measure of electron density; however, it is proportional to the force constant, and thus should reflect changes in electron density at the carbonyl site.

In this work we have used standard alkali metal reduction techniques in dimethoxyethane (used previously for epr studies) in conjunction with NaCl cavity cells of 0.05-mm width. In all cases measurements were made using matched cells. Concentrations usually were in the range of 5 (±5) × 10^{-2} *M*. Occasionally it was necessary to use diluted samples around 10^{-4} *M*, but this required opened slits and increased source intensities on the instrument in order to obtain useful information.

The lithium reductions were performed with lithium amalgam; Na and K were distilled into the sample tube. Observations of the ketyls have been carried out at room temperature and measurements were made on Beckman IR-5 and Perkin-Elmer 21 and 521 instruments. Table I indicates the frequencies of the unreduced species, the observed frequencies of ketyls, the Hammett σ values (see discussion below), and the frequency difference between unreduced and reduced species. Figure 1 indicates a plot of σ_R^+ *vs.* $\bar{\nu}$ (ketyl) values. Figure 2 shows the plot of σ_R^+ *vs.* $\Delta\bar{\nu}$ (the difference between the parent ketone and the ketyl).

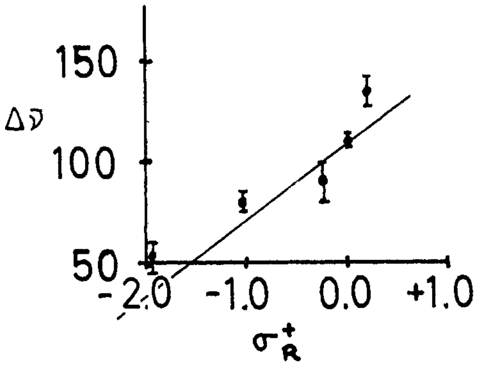

Figure 2.

Choice of σ Values.—Only those ketones which would not tend to decompose upon metal reduction at room temperature were chosen for study; of these, only two of the five aromatic compounds studied are not susceptible to resonance interaction. In view of the fact that ketyls are essentially anion radicals, we found it desirable to use the σ_R^+ values determined for the cation radicals of *N*,*N*-dimethylaniline as determined by Latta and Taft.[7] As these authors mention, their results for σ are similar to those used for anion radicals by Strom.[8] Strom, however, used σ_P parameters from Brown and Okamoto[9] which do not reflect problems in resonance interaction between the para substituent and the measuring site. We have plotted the σ_P values also (circles, in Figure 1). A linear relationship is obtained with these values; nevertheless, we feel that the σ_R^+ parameters ($\sigma_R^+ = \sigma_P - \sigma_I$) of Latta and Taft are more applicable in our case. We are using single σ values, although to be more exact it might be more appropriate to double the σ values, since there are two substituents affecting the measuring site.

An interesting comparison of hyperfine splittings (hfs) with three 4,4′ substituents can be seen in Table II. Here we see that the spin density (as reflected by hfs) upon the aryl rings is increasing with increasing electron donation. Epr results are not available for $-N(CH_3)_2$ and $-NO_2$ substituents. Since a significant portion of the spin density in the $-NO_2$ substituted ketyl probably resides in that substituent, comparison of hfs for that ketyl would not be realistic, heeding Janzen's *caveat* for that situation.[10] This means, of course, that the spin density at the carbonyl site must be *decreasing*. This observation is in line with the results plotted in Figure 2; *i.e.*, the more negative σ values result in less perturbation of the carbonyl stretching frequency.

It has been suggested to us that inclusion of ir data from 4,4′-disubstituted phenyl nitroxides might be instructive. This has not been included for two reasons. At present there exist no such data, although we are attempting to secure it. Further, nitroxides represent a class of compounds in which the odd electron is in a nonbonding situation, and thus cannot reasonably be compared with a charge species which bears the odd electron in an antibonding orbital and which also has a closely associated positively charged metal ion. Some correlations of the N–O stretching frequency of substituted pyridine *N*-oxides with Hammett σ values have been made,[11] but, again, *N*-oxides of tertiary amines do not represent a bonding situation comparable to that of ketyls. We would like, in addition, to emphasize that Figures 1 and 2 do not represent an attempted strict Hammett-type correlation of free energy values, but rather do demonstrate a definite trend toward lowered frequencies upon increasing electron withdrawal at the ketyl site by whatever means, inductive, resonant, or both.

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[4] D. H. Eargle, Jr., and E. W. Cox, "The Alkali Metals," Special Publication No. 22, The Chemical Society, London, 1967, pp 116–124. (Typical spectra are published here.)

[5] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2811 (1962).

[6] D. H. Eargle, Jr., Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967, pp 55–60; *J. Chem. Soc.*, in press.

[7] B. M. Latta and R. W. Taft, *J. Amer. Chem. Soc.*, **89**, 5172 (1967).

[8] E. T. Strom, *ibid.*, **88**, 2065 (1966).

[9] H. C. Brown and Y. Okamoto, *ibid.*, **80**, 4979 (1958).

[10] E. G. Janzen, *Accounts Chem. Res.*, **2**, 282 (1969). "When a large fraction of the total spin density is localized on any substituent, Hammett relationships break down."

[11] E. Ochiai, "Aromatic Amine Oxides," Elsevier, New York, N. Y., 1967, pp 122–126.

TABLE I

4,4′-DISUBSTITUTED BENZOPHENONE KETYL FREQUENCIES

Substituent	Registry no.	$\bar{\nu}_{\text{ketone}}$, cm^{-1}	$\bar{\nu}_{\text{ketyl}}$, cm^{-1a}	$\Delta\nu$	σ_R^{+b}	σ_P^c
$N(CH_3)_2$	90-94-8	1650 ± 2	1585 ± 5	65 ± 7	−1.97	−0.83
OCH_3	90-96-0	1660 ± 5	1580 ± 5	80 ± 6	−1.03	−0.27
CH_3	611-97-2	1660 ± 2	1568 ± 5 (K^+) 1572 ± 1 (Na^+) 1575 ± 2 (Li^+) concd and dilute	92 ± 7	−0.26	−0.17
H	119-61-9	1664 ± 1	1554 ± 2 (K^+, Na^+) 1563 ± 2 (Li^+) concd (dimer) 1617 ± 3 (Li^+) dilute (monomer)	110 ± 3	0.00	0.00
NO_2	1033-26-7	1670 ± 2	1535 ± 5	135 ± 7	+0.18	+0.78
Di-*tert*-butyl ketone	15796-82-4	1689 ± 2	1558 ± 2	131 ± 4		

[a] Several of our values in dimethoxyethane differ somewhat from those determined in CCl_4 by Fuson, *et al.* (ref 3). [b] See ref 7. [c] See ref 9.

TABLE II

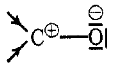
4,4′-DISUBSTITUTED BENZOPHENONE Hfs[a]

Substituent	Position			σ_R^+ (ref)	ρ(aryl) Q = −23.5 G
	ortho	meta	para		
OCH_3	2.78	−0.99	0.27(OCH_3)	−1.03 (7)	
CH_3	2.73	−0.91	3.64(CH_3)	−0.26 (7)	0.62
H	2.52	−0.82	3.50	0.00 (7)	0.59
Cl	2.5	−0.84		0.08 (9)	

[a] P. L. Nordio, G. Giacometti, and P. Favero, *Ric. Sci. Parte 2 Rend. Sez. A*, **3**, 107 (1963).

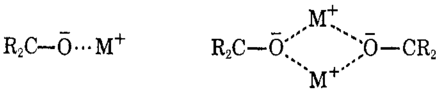
Discussion

Regardless of the set of σ values used, the most startling feature of the results is the *decrease* in ketyl stretching frequency corresponding to an increase in the electron-withdrawing power of the substituent. The carbonyl stretching frequencies of the unreduced benzophenones reflect fairly well the expected variations with substituent electron donation[11] weakening the C–O bond by stabilizing the structure



In Figure 2 is plotted the *difference* in the ketone and the ketyl stretching frequencies ($\Delta\nu$) *vs.* the σ_R^+ values. These differences become progressively larger with the greater electron-withdrawing power of the para substituent. Thus, both the results of Figures 1 and 2 are disquieting in that neither reflects what might have been predicted, that is, that the ketyl C–O bond should become tighter with an increase in the value of σ as in the ketones. The results appear to say that electron-donating groups, instead of further loosening the C–O bond, actually strengthen it.

At this point it should be noted that we are probably observing the stretching frequency of a metal–ketyl dimeric ion pair II, studied originally by Hirota,[12–14] rather than the monomer I. Hirota's work shows that at lower concentrations (~10^{-5} *M*) the metal ion is



I II

R = aryl or *tert*-butyl

highly solvated and causes only weak, if any, epr hyperfine splittings. However, at concentrations near 10^{-2} *M* the metal hyperfine splittings are quite pronounced and the epr studies show unequivocally that form II predominates (in dimethoxyethane) and that the metal–oxygen nuclear distance is only about 2 Å.[13b] Since our concentrations range from about 10^{-1} to 5×10^{-2} *M*, we are no doubt observing phenomena due to these dimeric ion pairs. It is not likely, either that we are observing pinacolate-type dimers; Hirota and Weissman[14] have shown spectrophotometrically that at 10^{-2} *M* concentrations in DME this dimer is present in negligibly small concentrations. With one exception we have found no observable change in the frequency of the ketyl upon dilution from concentrations of ~10^{-2} *M* to ~10^{-4} *M*. Were the species under observation to markedly change its degree of solvation, we should expect a change towards a different frequency upon progressive dilution. Only in the case of benzophenone do we observe an abrupt change of frequency upon extreme (>10^{-4} *M*) dilution; however, the color of the material also changes, indicating that we are observing a change from the dimer (purple) to the monomer (blue), as reported by Hirota's study of the visible spectra.[13a] Therefore, we must conclude that the lack of frequency (and color) changes in the higher concentration ranges indicates that either we are observing the same species throughout the dilution process, or the ir spectrometer is too insensitive to detect a change.

The effect of the nature of the alkali metal also bears upon this point. There is little or no difference (within experimental error) of the ketyl absorptions of the K^+ and Na^+ counterions (see Table I), a fact which again strongly implies, as does Hirota's epr study, that there is little difference in structure between Na^+ and K^+ ketyls. Yet, when we go to the Li^+ counterion we should expect a more tightly held ion pair. If our hypothesis of counterion assistance is correct, a more

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[12] Several of our values in dimethoxyethane differ somewhat from those determined in CCl_4 by Fusion, *et al.* (ref 3).

[13] (a) N. Hirota, Ph.D. Thesis, Washington University, 1963. University Microfilms, Inc., Ann Arbor, Mich., No. 64-2316; T. Kaiser and L. Kevan, "Radical Ions," Interscience, New York, N. Y., 1968, Chapter 2. (b) Reference 13, p 68.

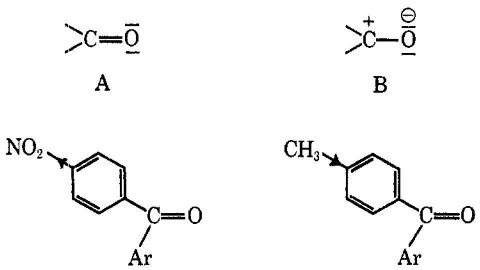
[14] N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **86**, 2538 (1964).

tightly held ion should serve to increase the C–O bond strength, as indeed Li^+ does, to the extent of 7–9 cm^{-1} in benzophenone and ditolyl ketone.

The ketyl of di-*tert*-butyl ketone (lifetime ~30 min) has been included in Table I for reference purposes. This ketyl represents one in which the odd electron is almost totally confined to the C–O site (Hirota reports little solvent or temperature dependence and a quite large metal hfs, resulting in a "tight" ion pair of structure II). Comparison of its frequency shift to those of its aromatic cousins demonstrates its similarity to the 4,4′-dinitro species.

The problem of describing these effects at the ketyl site is, simply stated, to devise a mechanism wherein the antibonding character of the odd electron may be increased, as reflected by a lower observed C–O frequency, or decreased, in the case of a higher one.

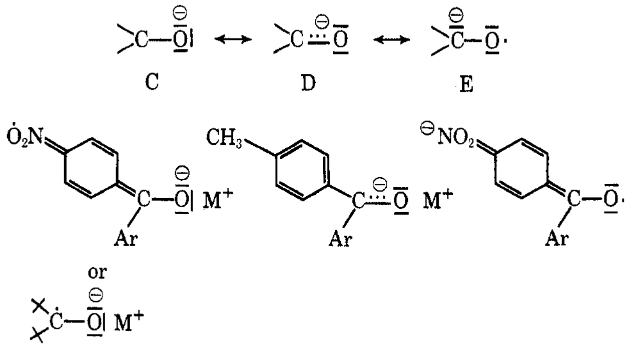
Valence bond structures may be invoked to describe the observed effects, but prove to be rather awkward in depicting all situations. The conventional resonance structures of the ketone (A, B) are adequate to describe the substituent effects of the unreduced ketone.



ketone structures with examples

In order to approach a depiction of the ketyl, Pauling's three-electron bond concept (his subterfuge for antibonds) must be summoned. Three contributing resonance structures of the ketyl may be shown by models C, D, and E. Electron-donating substituents can be seen to increase the probability of structure D, in which the resident electron density on the ketyl is greater than that of either C or E. In structure D we should expect some influence of metal counterion and also an increased C–O bond strength with increased electron donation, as borne out by experiment (see *p*-tolyl, Table I).

Since *p*-tolyl benzophenone ketyl possesses a higher frequency than benzophenone ketyl (and neither has large substituent resonance effects), it must be assumed that the counterion effect is stronger in the former and, at the same time, allows more delocalization of the odd electron (see Table II). This is reasonable, since electron-donating groups would certainly increase the entire electron density at the ketyl site.

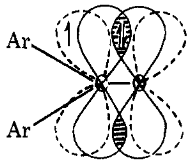


ketyl structures with examples

Electron-withdrawing substituents such as NO_2 cause structure C or E to predominate. The similarity in stretching frequency of 4,4′-dinitrobenzophenone ketyl and di-*tert*-butyl ketyl can be rationalized by involving only structure C, in which very little delocalization of either charge or spin can occur and in which counterion influence must be large, giving the known "tight" ion pair.

A partial MO description (F), while possessing some defects, can perhaps characterize the situation in MO terms in which the bonding π orbitals between C and O are occupied as well as the nonbonding orbitlas of oxygen (not shown). The antibonding orbitals between C and O are also occupied, by the odd electron, which upon the influence of electron donation by Ar is more likely to be found on the central carbon atom, while the charge density is increased on the oxygen. Electron withdrawal by Ar results in a greater influence in antibonding by the odd electron and at the same time possibly allows enhanced bonding of the metal–oxygen pairs.

bonding π orbitals (solid lines)



antibonding π orbitals (dotted lines)

F

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