Anionic Hyperconjugation: The Infrared Spectra of Sodium Alkoxides

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Stabilization by anionic hyperconjugation of alkoxide ions containing *alpha* hydrogen atoms is strongly indicated by shifts in the infrared absorption in the 2500–3000 cm.$^{-1}$ region observed in several alcohol-sodium alkoxide pairs. The shifts become progressively larger in the sequence methyl, ethyl, and isopropyl, and substantially vanish with *tert*-butyl. Comparison with the magnitude of inductive and steric influences in analogous series of compounds further indicates that this resonance stabilization exerts a controlling influence on the acidities of these aliphatic alcohols. A powerful driving force, such as that supplied by the negatively charged oxygen atom, appears to be necessary for this type of resonance to be of appreciable significance.

In addition to the generally recognized hyperconjugation in which electron release by, usually, a carbon-hydrogen bond gives a canonical structure with a non-bonded proton, hyperconjugation involving structures in which the hydrogen atom accepts the bonding electrons appears to be of importance. The nature of this effect makes its detection by physical means generally difficult. There are, however, chemical data which are most easily understood in terms of this "anionic" hyperconjugation.

Studies of the acidity of aliphatic alcohols, although not providing absolute values for the acidities, do yield comparative data for the effects of structural changes. Consideration of these relative acidities suggests the presence of an anionic hyperconjugation effect. This conclusion is supported by the data to be presented in this paper. Electronic, steric, and solvating effects cannot, of course, be ignored, and are evaluated in a later section.

Table I gives the pK_a values of McEwen[2] and the K_e values reported by Hine[3] for a series of alcohols. Although the data of McEwen are only order of magnitude values and those of Hine are not applicable to acids weaker than ethanol, the large decrease in acidity accompanying the substitution of methyl groups for the *alpha* hydrogen atoms is evident. These data are in accord with the striking 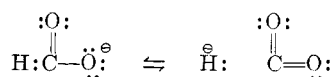decrease in reactivity toward sodium observed qualitatively in the series methyl, ethyl, isopropyl, and *tert*-butyl alcohols.

These observed acidities can not be understood satisfactorily on the basis of an inductive effect. The data of Table II show the magnitude of the change observed in similar situations in which the inductive effect is the important factor operating. The substitution of carbon for hydrogen in formic acid and ammonia brings about a large change, but further alteration of this group has little effect, much less than is apparently the case in the alcohol series. Thus variations in acidity and basicity produced by an inductive mechanism are seen to be much smaller than the effects shown in the examples of Table I.[4]

The possible influence of solvation on the acidities of these compounds must also be considered. Variation in solvation is an important factor in the basicities of primary, secondary, and tertiary amines.[5] This follows, presumably, from the association of the oxygenated solvents with the hydrogen atoms bonded to nitrogen. In the present case, however, the important solvating group of the alcohol or alkoxide is unchanged throughout the series. Although the total number of solvent molecules grouped about the ion may change as the size of the ion increases, the important solvation is *via* hydrogen bonding, and only one molecule at a time can be important in this respect. Thus it appears that no significant difference in acidity can be ascribed to change in solvation with change in the substituent.

The effect of steric strain on the alcohol acidities is next to be considered. It might be argued that steric pressure would make loss of a proton easier from *tert*-butyl alcohol than from methyl alcohol. The trend, however, is clearly in the opposite direc-

TABLE I
RELATIVE ACIDITIES OF ALCOHOLS

Alcohol	pK_a	K_e
Methyl	16^a	4.0
Ethyl	18	0.95
n-Propyl	—	.5
Isopropyl	18	.076^b
sec-Butyl	—	<.2
tert-Butyl	19	<.2

^{a} Assumed standard for the series. ^{b} Set by the experimental conditions.

(1) Present address, Brea Chemicals, Inc., Brea, California.

(2) McEwen, *J. Am. Chem. Soc.*, **58**, 1124 (1936).

(3) Hine and Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(4) The referee has suggested that anionic hyperconjugation may make an important contribution to the acidity of formic acid, *i.e.*

$$H:\overset{:O:}{\underset{\cdot\cdot}{C}}-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:{}^{\ominus} \quad \leftrightharpoons \quad \overset{\ominus}{H}: \quad \overset{:O:}{C}=\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$$

(5) Pearson and Williams, *J. Am. Chem. Soc.*, **76**, 258 (1954).

TABLE II
IONIZATION CONSTANTS OF ACIDS AND BASES

| R		H	CH₃	CH₃CH₂	(CH₃)₂CH	(CH₃)₃C
RCOOH	$(10^5 K_a)^a$	20.0	1.75	1.33	1.38	0.89
p-RC₆H₄COOH	$(10^5 K_a)^a$	6.67	4.24	—	—	4.2
RNH₂	$(10^4 K_b)^b$	0.18	3.5	4.9	4.0	5.0

[a] Dippy, *Chem. Revs.*, **25**, 151 (1939).   [b] Pearson and Williams, *J. Am. Chem. Soc.*, **76**, 258 (1954).

tion. Furthermore there is evidence that in simple cases there is little if any steric acceleration in ionization processes, such as, for example, the solvolysis of ethyl and neopentyl bromides in formic acid.[6]

The most reasonable explanation remaining to account for the observed differences in acidity of the alcohols is a resonance stabilization of the alkoxide ions of such nature as to be relatively unimportant in the alcohols themselves. This explanation has been advanced,[3] but no definite evidence has been put forward in support of it. Anionic hyperconjugation as illustrated below requires first the presence of *alpha* hydrogen atoms and second the potent driving force of the negatively charged oxygen.
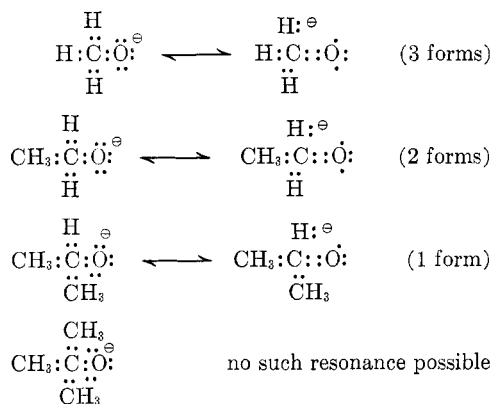
Further chemical evidence for the importance of such structures is the proposal of direct donation of a hydride ion by an alkoxide ion to a carbonyl compound as the most satisfactory explanation of observations on the carbinol-carbonyl equilibrium.[7] Such conjugation is analogous to, though less to be expected than that proposed by Roberts[8] to explain the directive effect of the trifluoromethyl group in aromatic substitution.
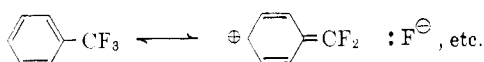
Support from physical or structural measurements for this suggested hyperconjugation has not been readily obtained. Since such an effect is likely to be important only in such substances as the alkoxides, the usual evidence on bond lengths and dipole moments is lacking. It appears, however, that the infrared spectra can provide the necessary support.

The resonance forms depicted suggest a weakening of the *alpha* carbon-hydrogen bonds and a corresponding strengthening of the carbon-oxygen bonds. In the 3000 cm.$^{-1}$ region, therefore, a shift to lower frequencies of the *alpha* carbon-hydrogen stretching bands might be expected. This shift would probably be greater for the isopropoxide with a single *alpha* hydrogen than for the methoxide, in which the hyperconjugation is spread among three carbon-hydrogen bonds. The strengthening expected from the increased electron density in the carbon-oxygen bonds of the alkoxides probably acts in opposition to a possible weakening brought about by the formal negative charge on oxygen.[9] In any event, the band shift in the skeletal region is likely to be obscured by the strong interaction between the carbon-oxygen and carbon-carbon stretching modes in the alkoxides other than the methoxide.

To test this hypothesis the infrared spectra of various alcohol-sodium alkoxide pairs were obtained as described in the experimental section. The spectra are shown in Figure 1, the significant frequencies being listed in Table III. Vertical comparison of the fourth and fifth columns shows that the predicted shifts have indeed occurred.

The shifts in the region of skeletal vibrations, 900–1100 cm.$^{-1}$, fall approximately in the expected order. Interpretation from these absorptions, however, is not profitable in view of the unknown effect of the negative charge on the oxygen atom. Only for the methanol-methoxide pair is the assignment of a fairly pure carbon-oxygen stretching frequency possible. In this case there is a very clear increase in frequency corresponding to the increased bond order of the carbon-oxygen linkage.

Since the spectra obtained were those of the alcohols as liquids and the alkoxides as solids, it is necessary to consider possible effects of the physical state on the infrared spectra. The alkoxides were run as mulls in various unreactive liquids and as KBr wafers. Since in any case it is the spectrum of the solid alkoxide that is obtained, no differences were expected or observed. More important is the possible effect of crystal structure on the spectra

(6) Dostrovsky and Hughes, *J. Chem. Soc.*, 164, 166, 171 (1946).

(7) Doering and Oschner, *J. Am. Chem. Soc.*, **75**, 393 (1953).

(8) Roberts, *J. Am. Chem. Soc.*, **72**, 408 (1950).

(9) Pauling, *Nature of the Chemical Bond*, Cornell University Press, Ithaca, 1942, p. 169.
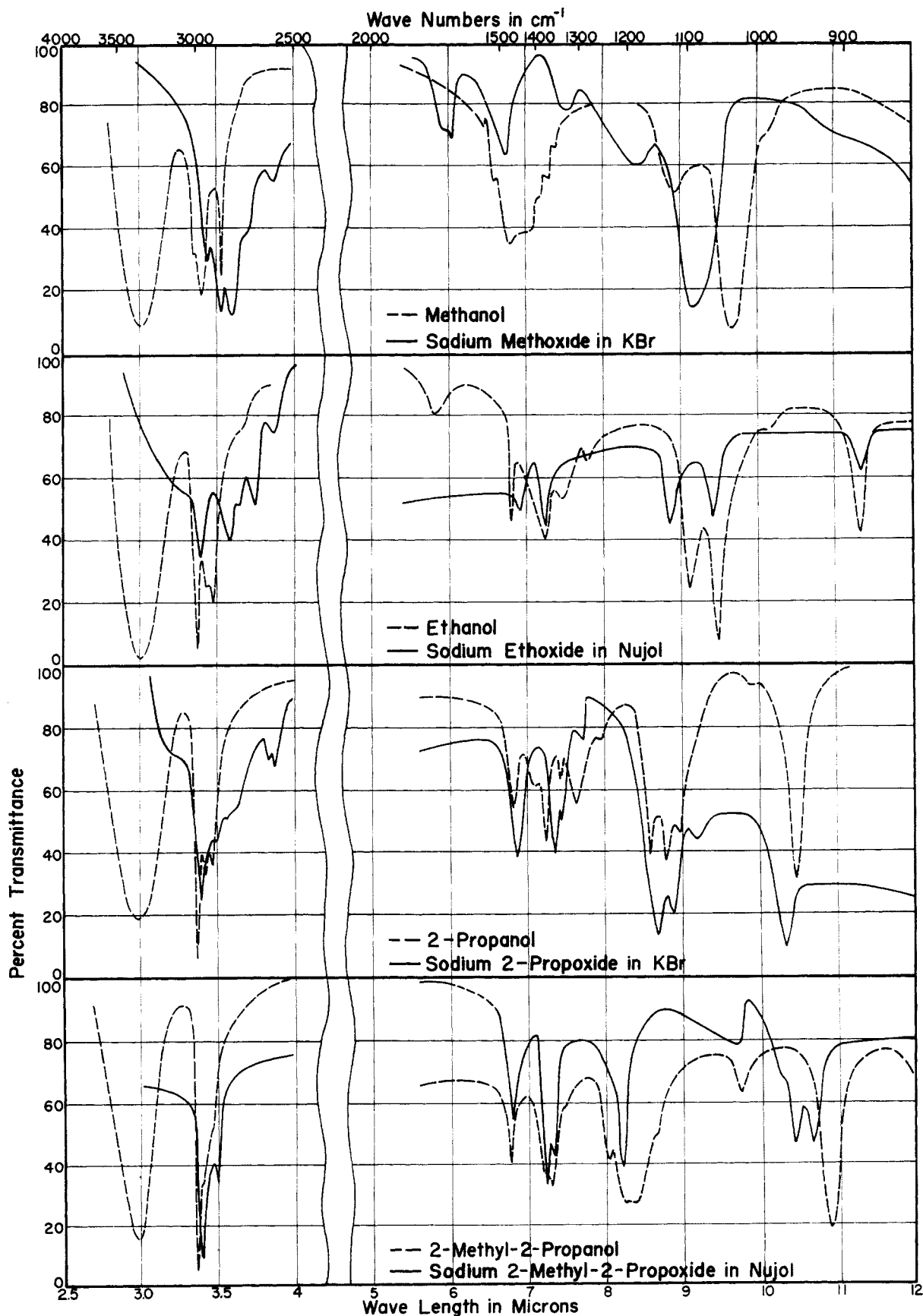
FIG. 1.—INFRARED SPECTRA OF ALCOHOL-SODIUM ALKOXIDE PAIRS.

TABLE III
INFRARED SPECTRA OF ALCOHOL-SODIUM ALKOXIDE PAIRS

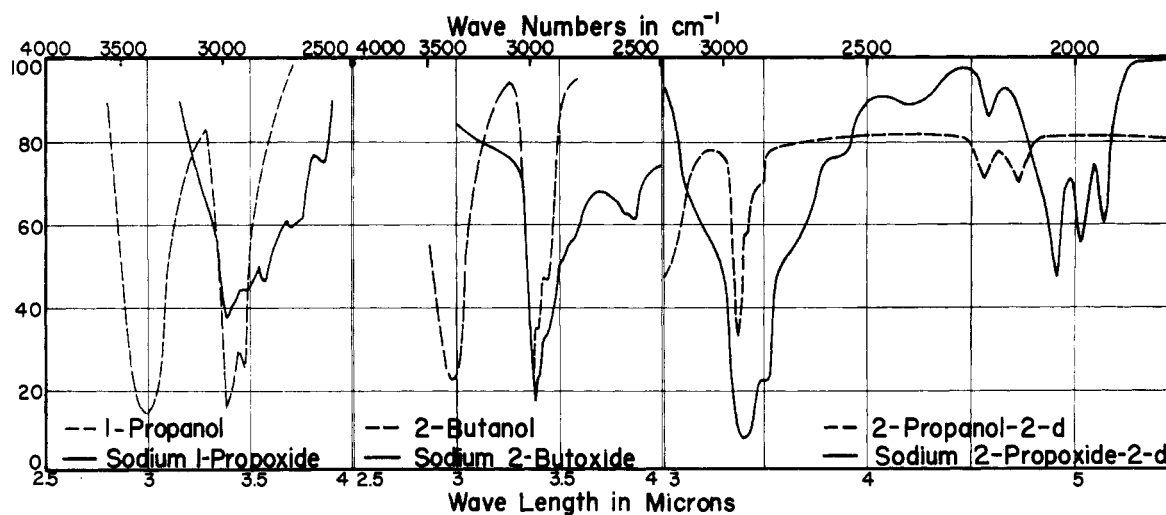| Alcohol	ν, ROH (cm.⁻¹)	ν, RONa (cm.⁻¹)	Skeletal region	Δ = νRONa − νROH, C—H stretching region αC—H	βC—H
Methyl	1035	1074	39		
	2994⎫	2916⎫			
	⎬2902	2843⎬2826		− 76	—
	2829⎭	2783⎭			
Ethyl	884	882	—		
	1055	1062	7		
	1097	1128	31		
		2581⎫			
	2899	2675⎬2675		−224	
		2799⎭			
	2968	2953			−15
Isopropyl	955	966	11		
	1136⎫				
	⎬1152	1149	—		
	1168⎭				
	2882⎫	2576⎫			
	⎬2906	⎬2596		−310	
	2923⎭	2612⎭			
	2965	2953			−12
tert-Butyl		936⎫			
	916	⎬945	29		
		956⎭			
	1197	1214	17		
	2968	2952		—	−16
n-Propyl		2591⎫			
	2879	2704⎬2704		−175	
		2804⎭			
	2961	2958			—
sec-Butyl	2877⎫				
	⎬2902	2592		−310	
	2928⎭				
	2962	2953			− 9
α-Deuterio-isopropyl	2110⎫	1942⎫			
	⎬2155	1984⎬1996		−159	
	2188⎭	2032⎭			
	2967	2941			−26

FIG. 2.—INFRARED SPECTRA OF ALCOHOL-SODIUM ALKOXIDE PAIRS.

of the alkoxides. Anomalous frequencies could arise from peculiarities of the packing of alkoxide and sodium ions. The set of molecules gives results, however, which fit into a regular pattern unlikely to result from such packing problems. Furthermore, although a comparison of the shifted *alpha* carbon-hydrogen bands of the alkoxides with those of the alcohols might be considered questionable, the treatment is entirely justified by the observed close coincidence of the *beta* carbon-hydrogen

bands of the alkoxides with the corresponding bands of the alcohols, 2955 ± 15 cm.$^{-1}$ (Table III, column 6). It is recognized, however, that for the carbon-oxygen absorption bands the interaction with the sodium ions will be more critical, and the frequency shifts may be more affected by crystal structure.

A further check that the physical state of the alkoxides is not responsible for the observed shifts is given by the spectra of lithium methoxide in various media (Table IV). These spectra reproduce in almost exact detail that of the corresponding sodium compound in both carbon-hydrogen and carbon-oxygen stretching regions. This congruence supports the view that the spectra here reported are those of the alkoxide ions and are not greatly dependent on interactions with the cation present.

TABLE IV

INFRARED ABSORPTION BY LITHIUM METHOXIDE IN VARIOUS MEDIA

Hexachloro- butadiene mull	Nujol mull	KBr wafer
1080	1080	1078
2930 ⎫		2930 ⎫
2840 ⎬ 2830	—	2840 ⎬ 2830
2790 ⎭		2790 ⎭

These spectra, therefore, provide new evidence for the existence of anionic hyperconjugation involving a hydride ion. There appears to be neither chemical nor physical evidence for conjugation with a methide ion. It would be expected that such a contribution would correspond to a greater shift in the carbon-hydrogen frequency in the *tert*-butyl alcohol-*tert*-butoxide pair than is actually observed. It is found, as expected, that isopropoxide

is more disposed to lose a hydride ion than is methoxide. The greater acidity of the latter, however, coincides with the greater stabilization due to the larger number of canonical forms available to it.

EXPERIMENTAL

Materials. Reagent grade alcohols were dried by refluxing over calcium oxide and then were distilled prior to use. The alkoxides were prepared by the addition of clean sodium to an excess of the alcohol under dry nitrogen. After solution of the sodium, the excess alcohol was evaporated at the full oil pump vacuum. The last traces of alcohol were removed by warming to 60–80° under a vacuum. The cooled alkoxides were stored under dry nitrogen. In this manner they could be kept relatively unchanged for several weeks, although all save the methoxide and *tert*-butoxide were most susceptible to oxidation by air, particularly if traces of alcohol remained in them.

α-Deuterioisopropyl alcohol was prepared by the lithium aluminum deuteride reduction of acetone. Its infrared spectrum in carbon tetrachloride solution agreed with that recorded in the National Bureau of Standards catalog. The sodium alkoxide was prepared by refluxing equivalent quantities of the alcohol and crushed sodium in dry hexane under nitrogen. After the sodium had reacted the solvent was evaporated as described above.

All operations with the alkoxides were carried out in a dry box filled with nitrogen.

Spectra. The alcohols were diluted with four volumes of dry carbon tetrachloride and their spectra were determined with a 0.03-mm. rock salt cell in a Beckman IR2T recording spectrophotometer using a rock salt prism over the whole range and a lithium fluoride prism in the 2500–4000 cm.$^{-1}$ range. As a single exception, the spectrum of α-deuterioisopropyl alcohol was determined at 1:10 dilution in a 0.10-mm. rock salt cell in a Baird Double Beam recording spectrophotometer with a rock salt prism.

The salts were examined as mulls, Nujol being employed in the range 800–1250 cm.$^{-1}$, hexachlorobutadiene in the range 1250–3000 cm.$^{-1}$. The latter agent was superior to the ordinarily used perfluorocarbon, which appeared to react with the isopropoxide and the *tert*-butoxide. Where noted, certain of the alkoxide spectra were also determined in KBr wafers, also using the Beckman instrument.

EVANSTON, ILLINOIS