A Nuclear Magnetic Resonance Study of Intermolecular Hydrogen Bonding in Nitromethane–Methanol Solutions

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Nitromethane (and other nitroalkanes) added to methanol with or without CCl_4 dilution suppresses exchange of the OH proton owing to the formation of strong intermolecular NO_2–HO hydrogen bonds. This prolonged residence time for exchange of the OH proton is sufficient to allow the detection of spin–spin coupling (J_{HCOH}) for the alcohol protons. The observed variability in the displacement of the OH resonance effected by CH_3NO_2 was interpreted in terms of complex formation. Extensive dilution studies (CCl_4) of CH_3NO_2–CH_3OH mixtures provided evidence for the formation of several discrete complexes of this donor–acceptor pair.

The nmr technique of using strongly hydrogen bonding solvents, *e.g.*, acetone, DMSO, or pyridine, for suppressing proton exchange in alcohols to allow the determination of J_{HCOH} has become a well-established procedure.[1] Although this phenomenon appears to be general for strong hydrogen bonding interactions between the OH and CO, SO, or trivalent N functions,[1] no prior reports of spin–spin coupling in alcohols induced by the NO_2 group, the observation of which prompted the present study, have appeared. Furthermore, the few reported studies of intermolecular NO_2–HO interactions,[2] which have been based primarily on the correlation of infrared OH frequency shifts ($\Delta\nu_{OH}$), indicate that hydrogen bonding interactions between nitro groups and the OH function of primary alcohols should be weak. This latter conclusion appears to be inconsistent with the strong intermolecular NO_2–HO interaction indicated by the present study.

Experimental Section

Instrumentation.—Nmr spectra were obtained at 27 ± 1° using a Varian A-60 spectrometer equipped with a variable-temperature probe. Chemical shifts were measured on the basis of separate determinations using the methyl resonance of methanol and 1–5% tetramethylsilane (TMS) as internal references; side-band techniques were used as a check. Calibration of the instrument was accomplished with an audio signal generator (Hewlett-Packard 205AG) monitored by a frequency counter (Hewlett-Packard 5244L) operated in the period mode. After warm-up, the drift and instability of the instrument were better than one part in 10^5. Spectrometer drift during 1 hr approached ±0.2 cps.

Sample Preparation.—High purity nitromethane was generously supplied by Commercial Solvents Corp. Methanol (Fisher Reagent Grade) was purified by distillation from magnesium methoxide, and stored over fresh $CaSO_4$ under nitrogen. Spectral Grade CCl_4 (Fisher) was stored over fresh $CaSO_4$ prior to use. No detectable impurities were apparent in the high gain nmr spectra of the materials used. Samples were prepared using standard volumetric techniques, as applicable. The volume or weight of the solvents was measured directly. Volumetric accuracies were ±1%; gravimetric accuracies were limited by evaporation of volatile solvent but approached ±0.3%. Temperatures were measured using a sealed sample of purified methanol.

Results and Discussion

Nitromethane added to methanol for the range of concentrations indicated in Figure 1 produced a 170.5-Hz extrapolated (143.2 Hz measured) upfield displacement, $\Delta\nu^{\infty}(CH_3OH–CH_3NO_2)$,[3] of the resonance position of the hydroxylic proton.[4] This marked displacement of the hydroxyl peak did not approach in magnitude the OH shift, $\Delta\nu^{\infty}(CH_3OH–CCl_4) = 292.8$ Hz,[3] reported for methanol diluted with CCl_4,[5] but greatly exceeded changes in the resonance position for the OH proton induced by acetone (91.5 Hz) or DMSO (48.0 Hz).[6] Variations in the hydroxyl proton shift of alcohols caused by the addition of strong hydrogen bonding acceptor species (acetone, DMSO) have been attributed to depolymerization of hydrogen bonded alcohol telomers and polymers and the inception of a hydrogen bonding association to the acceptor molecule.[1,5] The latter provides only a partial explanation for the results reported below.

The postulation of a strong intermolecular NO_2–HO interaction between nitromethane and methanol was supported by specific spectral changes noted on addition of the nitroalkane (Figure 2). Methanol containing low concentrations of nitromethane showed three broadened singlets (Figure 2a) in the nmr spectrum at τ 5.28, 5.65, and 6.64 ppm; the low- and high-field peaks showed relative intensities of 1:3, assignable to the hydroxyl and methyl resonances. At $[CH_3NO_2]/[CH_3NO_2] + [CH_3OH] = 0.4$ (approximately) spin–spin interaction ($J_{HCOH} = 5.2$ Hz)[7] was observed (Figures 2b and d) and was apparent in the methanol spectrum of all solutions containing higher nitromethane concentrations, *i.e.*, except at $[CH_3NO_2]/[CH_3NO_2] + [CH_3OH] = 0.75$ (approximately). Here, the alcohol resonances coalesced to a singlet. Thus, consistent with the changing $J/\Delta\nu$ ratio, as the OH peak moved upfield[7], the CH_3OH spectrum showed an AX_3 pattern, changed to A_3B and A_4 patterns, and finally reverted to an A_3X pattern as the OH proton resonance appeared at *ca.* 57 Hz (limiting observed shift) upfield of the methyl resonance. The cited spectral changes are consistent

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[1] Recently reviewed by P. Laszlo in "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. III, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, London, 1967.

[2] (a) W. F. Baitinger, P. von R. Schleyer, T. S. S. R. Murty, and L. Robinson, *Tetrahedron*, **20**, 1635 (1964); (b) Y. S. Su and H. K. Hong, *Spectrochim. Acta*, **24**, 1461 (1968); (c) H. E. Ungrade, E. M. Roberts, and L. W. Kissinger, *J. Chem. Phys.*, **68**, 3225 (1964).

[3] Throughout this communication, $\Delta\nu^{\infty}(CH_3OH–CH_3NO_2)$ and $\Delta\nu_{\infty}$ $(CH_3OH–CCl_4)$ signify the extrapolated or infinite dilution shifts (hertz at 60 MHz) for the **OH** proton of methanol in the indicated solvent. $\Delta\nu(CH_3OH–CH_3NO_2)$ and $\Delta\nu(CH_3OH–CCl_4)$ refer to observed shifts.

[4] The initial addition of CH_3NO_2 produced a 1.8-Hz downfield shift of the $-CH_3$ peak of methanol; thereafter, the methyl resonances were essentially invariant in position.

[5] (a) M. Saunders and J. B. Hyne, *J. Chem. Phys.*, **29**, 1319 (1958); (b) A. D. Cohen and C. Reid, *J. Chem. Phys.*, **25**, 790 (1956).

[6] W. Drinkard and D. Kivelson, *J. Phys. Chem.*, **62**, 1494 (1958). The values cited are corrected to 60 MHz.

[7] D. Kivelson and M. G. Kivelson [*J. Mol. Spectrosc.*, **2**, 518 (1958)] also reported $J_{HCOH} = 5.2$ Hz and a complete interpretation of the spectral changes encountered in the acetone–methanol system; W. B. Moniz, C. F. Poranski, Jr., and T. N. Hall [*J. Amer. Chem. Soc.*, **88**, 190 (1966)] have reported the solvent dependency of this parameter for various alcohols.

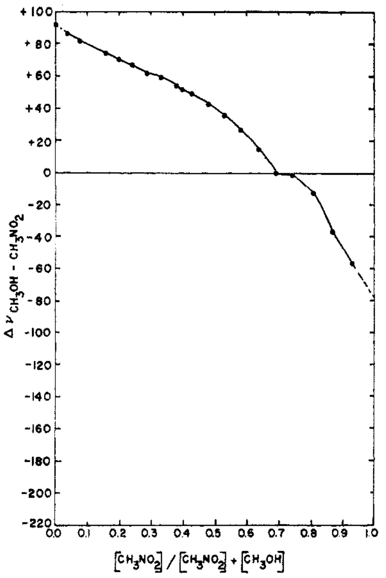

Figure 1.—Effect of CH_3NO_2 on Δν (CH_3OH). Negative values correspond to shifts of the OH proton upfield of the CH_3 resonance of methanol.

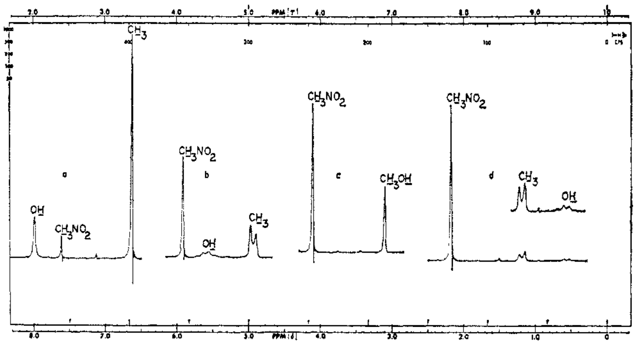

Figure 2.—Nmr spectra of CH_3OH–CH_3NO_2 mixtures at $[CH_3NO_2]/[CH_3OH] + [CH_3NO_2]$ equal to (a) 0.08, (b) 0.48, (c) 0.75, and (d) 0.87.

with reported studies of methanol and other alcohols for interactions with strong hydrogen bond acceptors (acetone, DMSO).[5-8] Clearly, the NO_2–HO bond formed between nitromethane and methanol is of sufficient stability to meet at least this nmr criterion for a strong hydrogen bonding acceptor, *i.e.*, the enhancement of the residence time for exchange of the hydroxyl proton.[1] The described phenomenon proved to be general for all nitro compounds tested, including nitroethane, 1- and 2-nitropropane, chloronitromethane, and nitrobenzene, which were studied only over limited concentration ranges in methanol. For each nitroalkane, coalescence of the methanol resonances was observed at nitroalkane concentrations approaching a molar excess. In comparison, the maximum possible shift induced by acetone (10 molar excess) was found to be 91.5 Hz (coalescence) in agreement with a prior study of this system.[6] Furthermore, the NO_2–HO bond formed is apparently highly stable to dilution since the addition of CCl_4 to solutions exhibiting splitting of the alcohol resonances shifted the **OH** resonance, but did not obliterate the patterns due to spin–spin interaction. This ability of the nitro group to retard exchange of the **OH** proton in dilute solutions has been rigorously tested in only one case, *i.e.*, nitromethane and methanol. Solutions of this donor–acceptor pair in CCl_4 at a total methanol concentration of less than 0.07 M[9] still showed splitting of the methanol resonances.[10] For nitromethane to induce this effect even in highly dilute solutions is clearly inconsistent with the weak hydrogen acceptor properties for this molecule previously reported.[2] Such weak intermolecular interactions are for the most part easily disrupted under these circumstances.

Previously, Krakower and Reeves[11] reported the observation of fine structure in the ambient temperature spectrum of a specially purified neat sample of methanol. The lack of observable splitting for the present methanol samples at low acceptor concentration might be attributed to acidic impurities or water; checks with carefully purified and degassed samples showed the probable cause to be low concentrations of adsorbed water.[12] Furthermore, an explanation for the observed splitting of the alcohol resonances based on scavenging of traces of acids or water would still require the assignment of strong hydrogen acceptor properties to the nitro group, in contrast to the weakly basic characteristics reported.[13]

An intriguing feature of the dilution curve (Figure 1) is the variability of the hydroxyl proton shift over the total range of nitromethane concentrations studied. Maxima in dilution curves, *e.g.*, Figure 1, centering at $[CH_3NO_2]/[CH_3NO_2] + [CH_3OH] = 0.50$ and 0.75 (approximately), have previously been cited as nmr evidence for complex formation between alcohols and strong hydrogen bonding acceptor species, *e.g.*, acetone;[6,14] only weak intermolecular complexes have been reported for nitroalkanes and alcohols on the basis of infrared studies.[2,15] However, since the formation of hydrogen bonded complexes between nitroalkanes and methanol might provide a consistent explanation for the present results, a more detailed nmr study of nitromethane induced shifts in the OH resonance was undertaken.

Contributions to Δν (CH_3OH–CH_3NO_2)[3] resulting from the autoassociation of either the proton donor or acceptor species were minimized by subjecting the CH_3NO_2–CH_3OH mixtures indicated in Figure 1 to a dilution series. For each CH_3NO_2–CH_3OH mixture (Table I) corresponding to the points indicated in Figure 1, dilutions were carried out using CCl_4 as the noninteracting solvent;[16] the displacement of the hydroxylic proton resonance, plotted *vs.* the volume increment of added inert solvent, gave the extrapolated or

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(8) O. L. Chapman and R. W. King, *J. Amer. Chem. Soc.*, **86**, 1256 (1964).

(9) At methanol concentrations less than 0.07 M, the **OH** quartet was barely visible above the background noise of our present instrument.

(10) The purified methanol used throughout this study did not exhibit spin–spin interaction in the nmr spectrum on dilution with CCl_4 to *ca.* 0.05 M; sufficient water was present to maintain rapid **OH** proton exchange in the absence of the nitroparaffin.

(11) E. Krakower and L. W. Reeves, *Trans. Faraday Soc.*, **59**, 2528 (1963).

(12) Rapid exchange of the **OH** proton was observed in the nmr spectra of nitromethane–methanol mixtures (undiluted or diluted with CCl_4) if the samples were not protected from atmospheric moisture.

(13) Reviewed by E. M. Arnett in "Progress in Physical Organic Chemistry," Vol. I, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Ed., Interscience Publishers, New York, N. Y., 1963.

(14) P. L. Corio, R. L. Rutledge, and J. R. Zimmerman, *J. Mol. Spectrosc.*, **3**, 592 (1959).

(15) M. S. Smith, Jr., and P. A. D. de Maine [*J. Miss. Acad. Sci.*, **12**, 97 and 109 (1966)] used a refined treatment of infrared data to obtain evidence for complexation between nitromethane and methanol.

(16) The major limitations to the use of carbon tetrachloride as an inert diluent have been thoroughly discussed by Laszlo.[1]

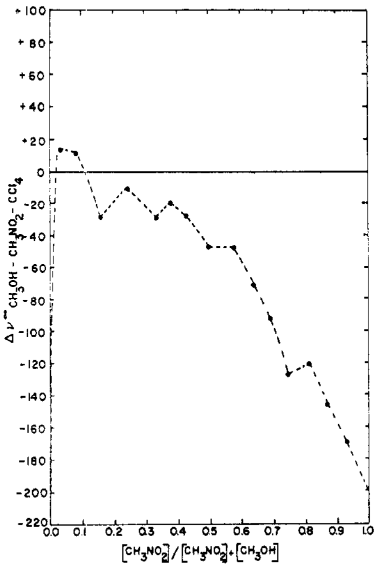

Figure 3.—The relationship between $\Delta\nu^{\infty}$ ($CH_3OH-CH_3NO_2-CCl_4$) and the nitromethane concentration. The CCl_4 concentration was assumed to be constant; only the concentrations of active species were considered in plotting the abscissa.

infinite dilution shifts of the OH proton, $\Delta\nu^{\infty}$($CH_3OH-CH_3NO_2-CCl_4$), for each mixture (Table I). The extrapolated shifts are plotted in Figure 3 to show the relationship to the relative concentrations of active species. Figure 3 is extrapolated at both ends to the corresponding infinite dilution shift, $\Delta\nu^{\infty}$($CH_3OH-CCl_4$) for the hydroxyl proton resonance of methanol in CCl_4, *i.e.*, 200 Hz upfield of the CH_3 resonance of methanol. This appeared to be a reasonable value for $\Delta\nu^{\infty}$($CH_3OH-CCl_4$) in view of studies carried out in our laboratories[17] and elsewhere.[5,18]

TABLE I

OBSERVED AND EXTRAPOLATED SHIFTS (HERTZ)[a] OF THE OH RESONANCE FOR $CH_3NO_2-CH_3OH$ MIXTURES

	$[CH_3NO_2]/[CH_3NO_2] + [CH_3OH]$	$\Delta\nu$ ($CH_3OH-CH_3NO_2$)	$\Delta\nu^{\infty}$ ($CH_3OH-CH_3NO_2-CCl_4$)[b,c]
1	0.038	+87.0	+12.0
2	0.075	+87.0	+15.0
3	0.158	+79.0	−31.0
4	0.245	+68.5	−10.0
5	0.332	+61.0	−31.0
6	0.381	+59.5	−20.0
7	0.429	+50.0	−30.0
8	0.520	+42.0	−48.0
9	0.582	+30.5	−49.0
10	0.663	+29.3	−72.0
11	0.668	+9.5	−96.0
12	0.749	−0.5	−126.0
13	0.810	−21.0	−120.0
14	0.870	−26.0	−146.0
15	0.937	−66.5	−170.0

[a] Internal shift of the OH resonance relative to the methyl resonance of methanol. [b] Extrapolation values were obtained from a series of five dilutions in CCl_4 for each $CH_3NO_2-CH_3OH$ mixture indicated. The total variation in the CCl_4 concentration was from 0 to *ca.* 90 mol %. [c] It should be noted that this abbreviation does not signify a constant, but depends upon the relative concentrations of active species.

A comparison of $\Delta\nu^{\infty}$ ($CH_3OH-CH_3NO_2-CCl_4$) and $\Delta\nu^{\infty}$ ($CH_3OH-CCl_4$) leads to some interesting and important conclusions regarding the $CH_3NO_2-CH_3OH$ interaction. The over-all high-field displacement of the OH resonance which occurred on diluting $CH_3NO_2-CH_3OH$ mixtures with CCl_4 (compared Figures 1 and 3) can be attributed primarily to disruption of the OH-O bonded structure of methanol;[1,5] the infinite dilution curve (Figure 3) should consequently trace the interaction of nitromethane and methanol monomers.[5] In the absence of any NO_2-OH interaction only dilution effects should be noted and $\Delta\nu^{\infty}$ ($CH_3OH-CH_3NO_2-CCl_4$) for each $CH_3NO_2-CH_3OH$ mixture studied (Table I and Figure 3) should approach $\Delta\nu^{\infty}$($CH_3OH-CCl_4$) as a limiting value; *i.e.*, Figure 3 would correspond to a straight line at *ca.* −200 Hz. This is clearly not the case and, excluding any marked effect of CCl_4,[18] the only reasonable explanation for the general downfield displacement of this curve [Figure 3 relative to $\Delta\nu^{\infty}$($CH_3OH-CCl_4$)] is the formation of strong NO_2-HO bonds, in support with the above conclusion based on the magnitude of $\Delta\nu^{\infty}$ ($CH_3OH-CH_3NO_2$) and the splitting of the alcohol resonances induced by nitromethane and other nitroalkanes.

Finally, the marked variability in the dependence of $\Delta\nu^{\infty}$ ($CH_3OH-CH_3NO_2-CCl_4$) on the relative nitromethane concentration, resulting in a series of maxima in Figure 3 at $[CH_3NO_2]/[CH_3NO_2] + [CH_3OH] = 0.05, 0.25, 0.33, 0.55$, and 0.75 (approximately), can be qualitatively, but reasonably, explained on the basis of two competing effects: (a) deshielding of the OH proton owing to the formation of NO_2-HO bonds between nitromethane and one or more methanol monomers, and (b) increase in shielding of the OH proton as the average number of methanol monomer units associated with nitromethane decreases.[19] Relative to $\Delta\nu^{\infty}$ ($CH_3OH-CCl_4$), the maximum displacement of the OH proton (*ca.* 210 Hz) occurring in Figure 3 at low nitromethane concentration ($[CH_3NO_2]/[CH_3NO_2] + [CH_3OH] =$ *ca.* 0.05) is already indicative of the formation of a strong NO_2-HO bond between these species. This conclusion is consistent with the sharply inclined initial slope of this curve[20] and the splitting of the methanol CH_3 resonance observed on diluting even these $CH_3NO_2-CH_3OH$ mixtures with CCl_4.[21] Past this initial maximum, the "average" slope of the curve is relatively shallow and can be accounted for by the balanced

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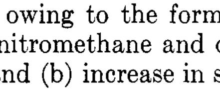
[17] A determination of the association shift for the methanol hydroxyl proton in our laboratories gave an extrapolated value of 293 Hz, in agreement with the Saunder's and Hyne value.[5]

[18] Whether the "high nitromethane" end of the curve for Figure 3 should be extrapolated to $\Delta\nu^{\infty}$($CH_3OH-CCl_4$) could not be unequivocally established in view of the present sensitivity limits of our nmr instrument, but this extrapolation is reasonable in view of other treatments of this data carried out in our laboratories. Total shifts due to the nonideality of CCl_4 as an inert solvent should be small, but in the same direction as the observed hydrogen bond shift.[5]

[19] The present data provide no clear indication of the nature of complex formation (see text); however, by invoking the formation of "bridged" and "open" hydrogen bonded complexes, *e.g.*, structures **1** and **2**, one might



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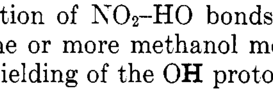

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anticipate increased shielding for the −OH proton in the bridged structure (**1**) relative to **2**.

[20] The slope of this curve at low CH_3NO_2 concentrations exceeds that for the $-OH\cdots O-$ interaction of methanol in CCl_4, *i.e.*, indicative of the formation of a stronger hydrogen bond in the $CH_3OH-CH_3NO_2$ system.

[21] On diluting this $CH_3NO_2-CH_3OH$ mixture with CCl_4, the CH_3- and −OH resonances for methanol were, respectively, a broad doublet and a very broad "lump," showing the presence of both bonded and exchanging alcohol species. It would appear that traces of nitromethane can retard −OH exchange for a relatively large number of methanol monomers.

but opposed shielding effects of hydrogen bonding and complex formation. Minima in Figure 3[19] corresponding to approximately 4:1, 2:1, and 1:1 complexes (OH–NO_2) appear indicative of some enhanced stability for aggregates having these stoichiometries. Above $[CH_3NO_2]/[CH_3NO_2] + [CH_3OH] = 0.5$, the definite increase in the slope of this curve would seem to corroborate the argument based on an increase in shielding for the OH proton in a 1:1 complex;[19] *i.e.*, if the increased slope of this curve at higher nitromethane concentrations were due simply to a dissociation of the NO_2–HO bonds, the disappearance of splitting patterns in the alcohol should also have been observed.[10]

To conclude these arguments supporting a strong NO_2–HO interaction, it is not difficult to explain the curvature deviations (Figure 3) in terms of discrete CH_3NO_2–CH_3OH complexes involving the nonbonding orbitals in the nitro group with one or more hydroxylic protons. However, the apparent minimum in this curve corresponding approximately to a 3:1 complex (NO_2–OH) is not readily explained in the absence of definitive evidence for NO_2–HC interactions.[22] Any participation of the CH protons of methanol in hydrogen bonding with a nitro group might be expected to result in some variation of the chemical shift for this peak. As noted above, neither of the CH_3 resonances in the spectrum exhibited a meaningful change in chemical shift (*i.e.*, >2.0 Hz)[4] relative to internal TMS over the entire range of concentrations studied. Thus, the observations reported here are consistent with a highly localized interaction between nitromethane and methanol. The nature of complex formation in this and other nitroalkane–alcohol systems is presently under study in our laboratories.

Attempts to compare the present results with nmr data available for other systems, *e.g.*, acetone or DMSO with methanol, have been inconclusive. It was possible to evaluate independently autoassociation effects for nitromethane and methanol, and apply empirical corrections to Figure 1;[23] the hypothetical curve obtained for the interaction of the monomeric species bore little resemblance to Figure 3 and the method was discarded. The present data are, in part, amenable to treatment using the Lussan method[24] for which the hydrogen bond shift (δ_B), crudely approximated by the difference $\Delta\nu^\infty$ (ROH–CCl_4) minus $\Delta\nu^\infty$ (ROH–CH_3NO_2), can be used to compare relative hydrogen bond strengths. δ_B shifts calculated for the CH_3OH–CH_3NO_2 and *t*-butyl alcohol–CH_3NO_2 systems are, respectively, 2.03[25] and 1.08 ppm,[24] in line with the increased steric effect expected with the latter alcohol. However, any firm comparisons regarding the nature of complexation and relative strengths of hydrogen bond formation in nitroalkane–alcohol systems will be reserved until the studies in progress are concluded.

There remains the apparent discrepancy which exists between infrared and nmr data with regard to the strength of the NO_2–HO interaction. On the basis of our studies in progress, it would appear that these differences arise in part from the practice of maintaining a relatively high excess of the nitro compound during the recording of infrared data. If, as the present nmr data indicate, the complexation of the nitroalkane and an aliphatic alcohol is a highly favored process, the small infrared OH frequency shifts noted for the interaction of these species may not be a reliable indication of this interaction.

Registry No.—Nitromethane, 75-52-5; methanol, 67-56-1.

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(22) A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 1715 (1963).

(23) B. B. Howard, C. F. Jumper, and M. T. Emerson, *J. Mol. Spectrosc.*, **10**, 117 (1963).

(24) C. Lussan [*J. Chim. Phys.*, **60**, 1100 (1963)] has calculated hydrogen bond shifts (δ_B) and equilibrium constants for complex formation in systems dealing mainly with 1:1 complexes.

(25) This study.