involving the nitrogen of the former N-oxide with C_1, and finally cleavage of the bond between C_2 and C_3 by a retrograde aldol-type condensation, all with appropriate isomerizations of the various enolic systems.

Acknowledgments. We wish to express our appreciation to our colleagues, Dr. P. Shu and staff for fermentations and large-scale concentration, Mr. L. Brancone and staff for microanalyses, Mr. W. Fulmor and staff for spectra and optical rotations, and Dr. J. Karliner for mass spectra.

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Proton Affinities of the Alkali Hydroxides

Sir:

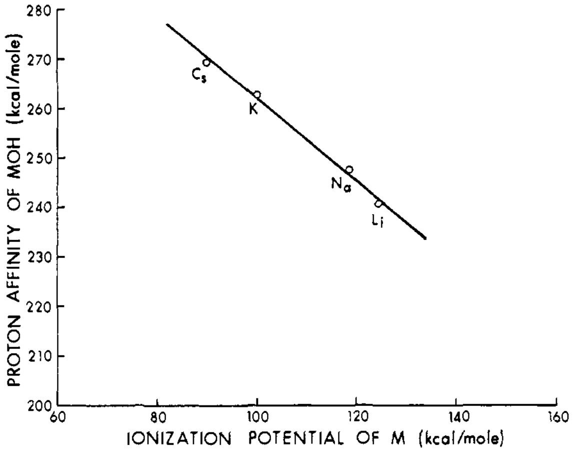

Figure 1.

Recent experiments in our laboratory have allowed measurements of the gas-phase equilibria of the reactions

$$M^+(OH_2)_{n-1} + H_2O = M^+(OH_2)_n \qquad (n - 1, n)$$

where M^+ is the alkali ion. These measurements allow the determination of $\Delta H_{n-1.n}$ and $\Delta S°_{n-1,n}$ which are of interest in a number of fields including that of ionic solvation. These data will be published in a separate paper.[1] The enthalpy changes $\Delta H_{0,1}$ relating to the reaction

$$M^+ + H_2O = (MOH_2)^+ \qquad (0,1)$$

when combined with available thermochemical data allow the determination of the proton affinities of the (gaseous) alkali hydroxides. These proton affinities which are of considerable chemical interest especially when compared to those of other related compounds are the subject of the present communication.

The proton affinity (PA) of the hydroxides, corresponding to the exothermicity of the gas-phase reaction (eq 1), can be evaluated from the enthalpy of formation

$$MOH + H^+ = (MOH_2)^+ \quad PA(MOH) = -\Delta H_1 \qquad (1)$$

of the reactants. The enthalpies of formation of MOH and H^+ are available. The enthalpy of formation of $(MOH_2)^+$ can be evaluated from reaction 0,1 since $\Delta H_{0,1}$ was determined and $\Delta H_f(M^+)$ and $\Delta H_f(H_2O)$ are available. Thus the proton affinity is given by eq

$$PA(MOH) = \Delta H_f(MOH) - \Delta H_{0,1} - \Delta H_f(M^+) + \Delta H_f(H^+) - \Delta H_f(H_2O) \qquad (2)$$

2. The results and the data used for their calculation are given in Table I. The values $\Delta H_f(H^+) = 367$ and $\Delta H_f(H_2O) = -57.8$ kcal/mole were also used.

The proton affinities of the hydroxides which are in the range 240–270 kcal/mole are considerably larger than those of water, methanol, and ammonia which are approximately 170, 185, and 216 kcal/mole, respectively.[2] It has been pointed out[3,4] that in the series R–OH the proton affinity should increase with the electron-donating ability of the substituent R. The very high proton affinity of the alkali hydroxides can be thus understood in terms of the very high electron-donating ability of the substituent M. This ability is so extreme that in the protonated species essentially all the charge resides in M; *i.e.*, the resulting structure is that of the hydrated alkali ion as indicated by the conventional formula $M^+ \cdot OH_2$.

The variation of the proton affinity in the MOH series with the electron-releasing ability of M is illustrated in Figure 1, where the proton affinities are plotted as a function of the ionization potential of the alkali atoms, the rationale of the plot being that the electron-releasing ability decreases with the ionization potential of the alkali atom. It can be seen that an almost linear relationship is obtained. Considering the proton affinity as a measure of the base strength of a (gas phase) Brønsted base, we find that the base strength of the hydroxides increases from Li- o CsOH. This order of

Table I. Proton Affinities of Alkali Hydroxides MOH and Thermochemical Data Used for Their Evaluation[a]

	$\Delta H_f(M)$	$I_p(M)$[b]	$\Delta H_f(M^+)$	$-\Delta H_{0,1}$[c]	$\Delta H_f(M^+H_2O)$	$-\Delta H_f(MOH)$	PA(MOH)
Li	38.0	124.3	162.3	34	71.3	55	240.7
Na	25.9	118.5	144.4	24.0	63.4	56	247.6
K	21.6	100.1	121.7	17.9	46.8	57.6	262.6
Cs	18.7	89.8	108.5	13.7	37.8	60.0[d]	269.2

[a] All values in kcal/mole refer to gas-phase species at 300°K. All data except $\Delta H_{0,1}$ taken from Vedeneyev, *et al.*[2] [b] $I_p(M)$ = ionization potential of M. [c] From ref 1. [d] Estimated from heat of formation of other alkali hydroxides.

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base strength need not be observed in solutions since there the process is complicated by solvation effects.

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Indirect Spin Saturation. IV.[1] The Effect of Saturating a Double Quantum Transition

Sir:

In nuclear magnetic resonance (nmr), transitions which are forbidden in the first order may be detected in the form of multiple quantum transitions at increased amplitude of the radiofrequency field.[2] The theory of multiple quantum transitions has been discussed by Yatsiv.[3] We wish to report here the effect of saturating a double quantum transition on the "normal" (single quantum) transitions. This effect can be applied to study relaxation and chemical exchange processes.

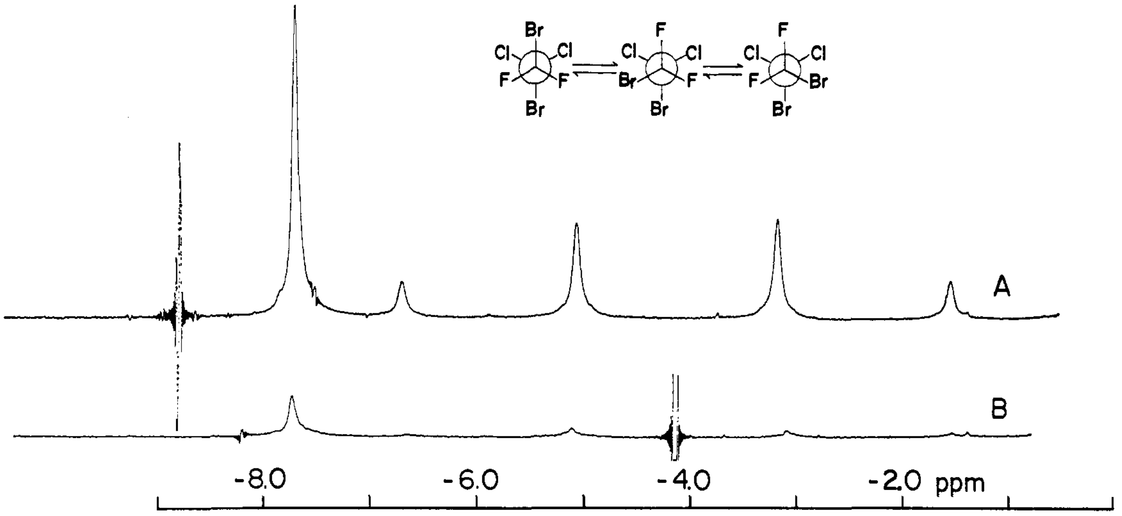

Figure 1. Fluorine-19 nmr spectra of 1,2-dibromo-1,1-dichloro-2,2-difluoroethane (mole fraction 0.15) in CS_2 at −80° and 94.077 MHz. α,α,α-Trifluorotoluene (mole fraction 0.05) was used as internal lock at 0.0 ppm. (A) The beat at −8.77 ppm, an irrelevant position, shows that a second stationary radiofrequency field was always on while sweeping the observing radiofrequency. (B) The beat at −4.09 ppm shows an irradiation at the double quantum transition of the AB quartet.

The direct saturation of an nmr transition by a strong radiofrequency field would equalize the populations of the spin levels connected by this transition. For an $I = {}^1/_2$, two-spin AB system, there is only one double quantum transition, namely $\alpha\alpha \rightarrow \beta\beta$. If the relaxation processes are not too fast, this transition can be completely saturated by a strong radiofrequency field. The saturation would make the populations of all four spin levels equal. The single quantum transitions are then saturated indirectly. Similar arguments can be extended to more complex spin systems. Experimentally, the system to be studied should have well-separated nmr peaks, so that the strong irradiation at the double quantum transition would not influence the signals directly. For proton resonance in liquid this is difficult to realize. In strongly coupled systems, the lines are close together; in weakly coupled systems where there may be well-separated groups, multiple quantum transitions are less favorable.[3] However, the effect of saturating double quantum transitions can be studied for proton resonance in liquid crystal, where the dipole–dipole interaction is large, or for fluorine resonance (in both liquid and liquid crystal), where there are large indirect spin–spin couplings.

The F^{19} nmr of 1,2-dibromo-1,1-dichloro-2,2-difluoroethane contains five peaks at low temperature[4,5] (Figure 1A). The two equivalent fluorine atoms of the *trans* conformer gave rise to a singlet at −7.70 ppm (*vs.* $C_6H_5CF_3$). The AB quartet centered at −4.09 ppm is due to the two fluorine atoms of the *gauche* conformers ($\delta_{AB} = 3.13 \pm 0.01$ ppm, $|J_{AB}| = 154.1 \pm 0.5$ Hz). The three conformers are in slow exchange because of the restricted rotation of the C–C bond. In order to avoid the change in the total intensity of the spectrum due to the turning on and off of a strong radiofrequency field ($\gamma H_2/2\pi \approx 27$ Hz in this case), the latter was set at an irrelevant frequency when the normal spectrum was recorded (Figure 1A). When the radiofrequency field was set at the frequency of the double quantum transition, the AB quartet was almost completely saturated (Figure 1B). In this system, there is another interesting feature in the spectrum. When the center of the AB quartet was irradiated, the singlet due to the fluorines in the *trans* conformer was also partly saturated: its peak area was reduced to 18 ± 2%. The saturation is caused by the transfer of demagnetization through chemical exchange.[6]

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