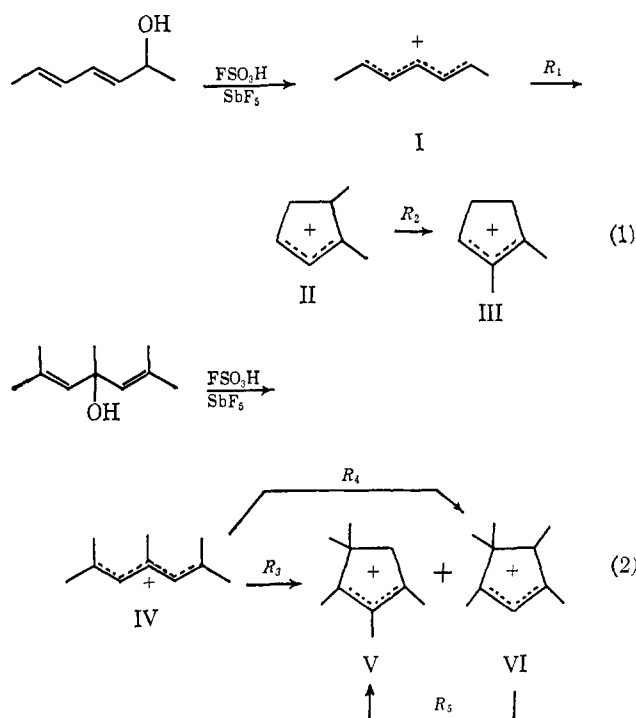Figure 1.

are sufficiently separated, timewise, so as to be considered as independent first-order reactions.

(1)

(2)

The nmr spectrum of I is shown in Figure 1. As in the case of other dienylic cations the conjugating hydrogens at C_2, C_4, and C_6 (−8.6 to 9.3 ppm, multiplet) are further downfield than the nonconjugating hydrogens at C_3 and C_5 (−7.41 ppm, triplet, J_{HH} = 13.5 cps).

Similarly (eq 2), IV is generated quantitatively in FSO_3H–SbF_5 at −60° and is stable for over an hour. At −30° V and VI are simultaneously and independently formed from IV ($t_{1/2}$ = 45 sec for disappearance of V), but a much higher temperature is required for conversion of VI to V (R_5 $t_{1/2}$ = 12 min at 27°). The independent formation of V and VI has been shown[3] but the ion IV has not previously been observed.[4]

The nmr spectrum of IV (Figure 2) demonstrates that all the methyl groups are deshielded to approximately the same degree (3.05 ppm, broadened).

Other trienes described previously[3] are now being studied in FSO_3H–SbF_5. The low-temperature capa-
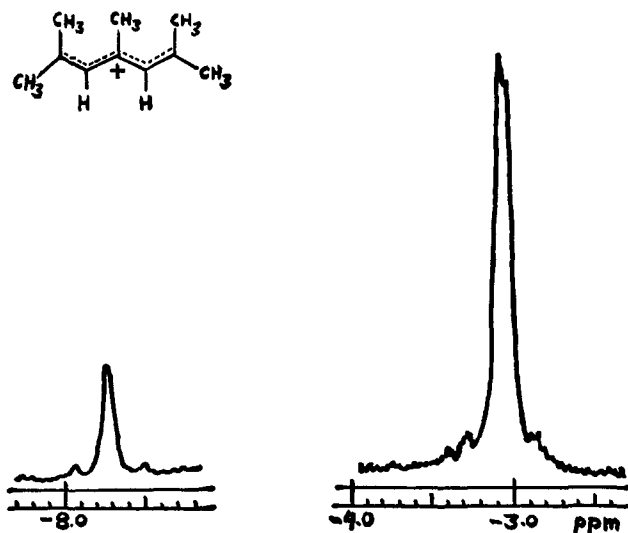

Figure 2.

bilities of this system allow one to observe dienylic open-chain cations which at higher temperatures undergo rapid rearrangement to mixtures of the more stable cyclized allylic ions.[3,4] The high acidity of this solvent also allows one to stablize and observe the intermediate ions in these cyclizations so that step by step detailed mechanisms may be elucidated.

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Rates of Proton Exchange between Dimethyl Sulfoxide and Its Conjugate Base

Sir:

The chemistry of dimethyl sulfoxide (DMSO) has been studied extensively. DMSO has proved to be an exceptional solvent for base-catalyzed reactions,[1] and its conjugate base ($CH_3SOCH_2^-$) has been used synthetically[2] as well as in quantitative measurements.[3,4] Protons adjacent to sulfoxide are known to exchange with base, and studies have been made in a number of systems.[5] Because of the great interest in the DMSO system, we have undertaken some quantitative rate

(1) D. J. Cram, B. Rickborn, C. A. Kingsbury, and P. Haberfield, *J. Am. Chem. Soc.*, 83, 3678 (1961); J. E. Hofmann, R. J. Muller, and A. Schriesheim, *ibid.*, 85, 3000, 3002 (1963); D. H. Froemsdorf and M. E. McCain, *ibid.*, 87, 3983 (1965).
(2) E. J. Corey and M. Chaykovsky, *ibid.*, 87, 1345 (1965).
(3) E. C. Steiner and J. M. Gilbert, *ibid.*, 85, 3054 (1963): 87, 382 (1965).
(4) A. Ledwith and N. McFarlane, *Proc. Chem. Soc.*, 108 (1964).
(5) D. J. Cram, W. D. Nielsen, and B. Rickborn, *J. Am. Chem. Soc.*, 82, 6415 (1960); E. J. Corey and E. T. Kaiser, *ibid.*, 83, 470 (1961); E. Buncel, E. A. Symons, and A. W. Zabel, *Chem. Commun.*, 173 (1965); A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *J. Am. Chem. Soc.*, 87, 5498 (1965).
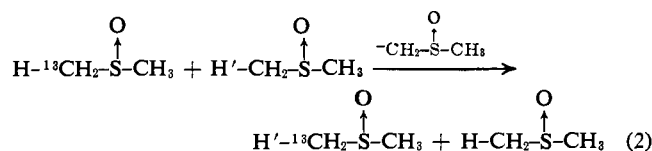
studies of the proton exchange. We wish to report a measurement of the rate of proton abstraction from DMSO by Na^+ and Li^+ $CH_3SOCH_2^-$.

In order to follow this reaction, a technique of general utility has been developed. The *proton* nmr spectrum[6] of DMSO consists of one peak (-2.5 ppm relative to TMS) with a pair of ^{13}C satellites, $J = 138$ cps. Since reaction of DMSO with $CH_3SOCH_2^-$[7] effectively causes proton exchanges between carbons, with increasing $CH_3SOCH_2^-$ concentration the satellites broaden and ultimately disappear.[8] For mean lifetimes between exchanges which are long compared with $\sqrt{2}/\pi J$ the rate of exchange can be determined from the half-width of the satellite according to eq 1.[9] Thus, it
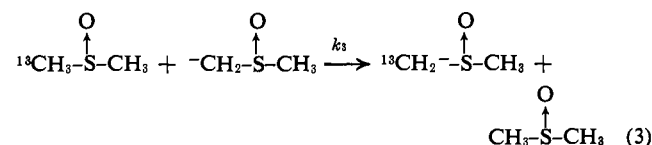
$$\frac{1}{T_2'} = \frac{1}{T_2} + k \qquad (1)$$

is possible to obtain kinetic information for systems which previously could not be analyzed.

The exchange process consists of proton interchange between ^{12}C and ^{13}C catalyzed by $CH_3SOCH_2^-$ (eq 2).

$$H-^{13}CH_2\overset{\overset{O}{\uparrow}}{S}-CH_3 + H'-CH_2\overset{\overset{O}{\uparrow}}{S}-CH_3 \xrightarrow{\overset{O}{\overset{\uparrow}{-CH_2-S-CH_3}}}$$

$$H'-^{13}CH_2\overset{\overset{O}{\uparrow}}{S}-CH_3 + H-CH_2\overset{\overset{O}{\uparrow}}{S}-CH_3 \quad (2)$$

If the rate-determining step is eq 3, and k from eq 1

$$^{13}CH_3\overset{\overset{O}{\uparrow}}{S}-CH_3 + {}^-CH_2\overset{\overset{O}{\uparrow}}{S}-CH_3 \xrightarrow{k_3} {}^{13}CH_2^-\overset{\overset{O}{\uparrow}}{S}-CH_3 +$$

$$CH_3\overset{\overset{O}{\uparrow}}{S}-CH_3 \quad (3)$$

is related by $k = k_3[CH_3SOCH_2^-]$, a plot of $1/T_2'$ vs. $[CH_3SOCH_2^-]$ should give a straight line with a slope of k_3.

This is indeed the case, and for base strengths from 0.1 to 0.8 M a bimolecular rate constant $k_3 = 12$ M^{-1} sec^{-1} was obtained for $Na^+CH_3SOCH_2^-$ at 37° assuming that the reaction is first-order in DMSO (see Figure 1).

The rate constant for $Li^+CH_3SOCH_2^-$, found by the same technique, is $k_3' = 7$ M^{-1} sec^{-1}. Thus, the lithium reaction is slightly, but measurably, slower than the sodium reaction. This may be associated with the increased viscosity of the lithium solutions.

The rates calculated in this way are the rates *per proton;* the chemical rate is six times as large.

(6) Spectra were determined on a Varian A-60 spectrometer, sweep width of 50 cps, with benzene added to solutions as a check on field homogeneity.

(7) Dimethyl sulfoxide was purified by distillation from calcium hydride. Solutions of $CH_3SOCH_2^-$ in DMSO were prepared on a vacuum line by transferring degassed DMSO to molecular sieves, then transferring to sodium hydride, lithium hydride, or butyllithium. Nmr tubes were sealed under vacuum, and the solutions appeared to be stable. Preparations carried out without the vacuum line gave identical results. Also see ref 2.

(8) Base concentrations were determined by titrating the contents of the nmr tubes for total base with potassium acid phthalate. Impurities more basic than $CH_3SOCH_2^-$ cannot be present due to the leveling effect of DMSO; impurities less basic probably would depress the rates, and we have observed this for some added substrates.

(9) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.
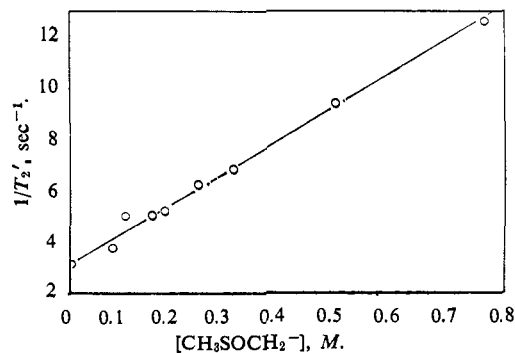
Figure 1. Half-width at half-height of proton resonance (^{13}C satellite) vs. concentration of $Na^+CH_3SOCH_2^-$.

The kinetic technique can be extended to determine rate constants at low base concentrations. The ^{13}C satellites are actually quartets, $J' = 0.45$ cps, due to long-range coupling with the protons (H_b) on the other methyl group. Collapse of the quartet arises because of exchange of protons H_b as well as H_a.

$$^{13}C(H_a)_3\overset{\overset{O}{\uparrow}}{S}-C(H_b)_3$$
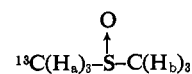
Although there is only one rate constant for exchange, there are statistically many different contributions to the collapse. The shape of the spectrum was analyzed as a function of the rate constant,[10] and rates were chosen to approximate collapse of the quartet. The rate constant for exchange with $Na^+CH_3SOCH_2^- \sim$ 0.08 M was found to be $ca.$ 10 M^{-1} sec^{-1}; that for Li^+-$CH_3SOCH_2^-$ was found to be $ca.$ 7 M^{-1} sec^{-1}.[11]

This is an extraordinarily fast proton transfer from carbon to carbon. More typically, for example, in ether, protons are transferred from fluorene to lithium fluorenyl with $k \cong 10^{-5}$ M^{-1} sec^{-1} at 25°.[12] On the other hand, proton transfers between oxygens or nitrogens are much faster, e.g., $k \cong 10^8$ M^{-1} sec^{-1} for protonation of methylamine by methylammonium ion.[13]

These results suggest that hybridization changes are indeed likely to be of great importance in proton transfer reactions.[14] Because extensive hybridization changes probably do not occur in the DMSO reaction, and because of the unique solvating properties of DMSO,[15] the reaction proceeds rapidly in spite of the very low acidity of DMSO. The greatly facilitated proton transfer in protic solvents must be partly a consequence of hydrogen bonded structures and pathways. The nmr of DMSO-$CH_3SOCH_2^-$ solutions shows no obvious evidence of hydrogen bonding.

The clean first-order dependence on base provides

(10) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 504. Details of these calculations will be published.

(11) The kinetic results by both techniques were reproducible, and acidic impurities (see ref 8) would necessarily have to be present in fortuitous amounts in each experiment to account for these results. In any case, the rates are almost certainly minimum values.

(12) J. I. Brauman and D. F. McMillen, unpublished results.

(13) E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, 27, 630 (1957).

(14) C. D. Ritchie and R. Uschold, *J. Am. Chem. Soc.*, 86, 4488 (1964).

(15) A. J. Parker, *Quart. Rev.* (London), 16, 163 (1962).

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a contrast to the work of Streitwieser,[16] and implies that in this system reversible polymeric association of base is relatively unimportant.

Finally, we would like to point out the significance of the satellite fine structure. A similar long-range coupling has been observed in acetone, $J = 0.54$ cps, and attributed to interactions with the π electrons of the carbonyl group.[17] The occurrence of this effect in DMSO may provide further indication of whether the electronic structure of the sulfoxide grouping should be best considered as an S–O double bond.[18]

Acknowledgment. We thank the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The Stanford University Computation Center generously provided a grant of computer time.

(16) A. Streitwieser, Jr., D. E. Van Sickle, and W. C. Langworthy, *J. Am. Chem. Soc.*, **84**, 244 (1962); A. Streitwieser, Jr., and W. M. Padgett, II, *J. Phys., Chem.*, **68**, 2919 (1964).
(17) J. R. Holmes and D. Kivelson, *J. Am. Chem. Soc.*, **83**, 2959 (1961).
(18) P. Haake, W. B. Miller, and D. A. Tyssee, *ibid.*, **86**, 3577 (1964).
(19) Stauffer Fellow, 1965–1966.

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Nondissociative First-Order Reactions of Some Metal Carbonyls

Sir:

This communication describes some preliminary results which are being reported at the present time because of possible widespread mechanistic significance in the interpretation of the substitution reactions of metal carbonyls.

Nickel tetracarbonyl was previously found to undergo radioactive carbon monoxide exchange in a reaction independent of ^{14}CO concentration.[1] Naturally, the $Ni(CO)_4$ was assumed to be reacting by a dissociative mechanism. This interpretation was apparently verified when the rate of reaction of $Ni(CO)_4$ with triphenylphosphine at 0° in toluene, also independent of phosphine concentration, was found to be about the same as the rate of ^{14}CO exchange.[2]

In a reinvestigation of these reactions, we have found that these two substitutions are separate processes. However, in agreement with earlier work,[1,2] both ^{14}CO exchange and reaction with triphenylphosphine or trimethyl phosphite were found to be first order in $Ni(CO)_4$ and zero order in the entering reagent. The values of ΔH^* and ΔS^*, listed in Table I for three solvents, are quite different for the two reactions, and the agreement in rates at 0° in toluene is entirely fortuitous.

As expected from the lower ΔH^* for ^{14}CO exchange, the ratio of the rate for ^{14}CO exchange to that for reaction with L decreases with temperature, and the ratio is less than 1 at 25° in toluene and heptane.

(1) F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961).
(2) R. F. Heck, *ibid.*, **85**, 657 (1963).

Similar observations have been made for exchange and substitution reactions of other metal carbonyls. For example, the rate of exchange of ^{14}CO with Hg-$[Co(CO)_4]_2$ is first order in the concentration of metal carbonyl but zero order in carbon monoxide. The activation parameters for exchange are $\Delta H^* = 13 \pm 1$ kcal/mole and $\Delta S^* = -24 \pm 2$ eu. Quantitative kinetic data could not be obtained on the reactions of $Hg[Co(CO)_4]_2$ with different phosphines and phosphites to form $Hg[CoL(CO)_3]_2$, but qualitative observations show that these reactions differ in mechanism from the CO-exchange process.

Table I. Activation Parameters for the Reaction of $Ni(CO)_4$ with ^{14}CO and L[a]

Solvent	—^{14}Co exchange— ΔH^*, kcal	ΔS^*, eu	—Reaction— with L[b] ΔH^*, kcal	ΔS^*, eu
Acetonitrile	10 ± 1	-36 ± 2	21 ± 1	2 ± 2
Toluene	12 ± 1	-26 ± 2	21 ± 1	2 ± 2
Heptane	10 ± 1	-36 ± 2	21 ± 1	1 ± 2

[a] L = triphenylphosphine or trimethyl phosphite; rate independent of L. [b] Similar results were obtained independently by R. J. Angelici and B. E. Leach (private communication) for L = $P(C_6H_5)_3$ in various solvents.

Also some of the results on the kinetics of exchange and substitution reactions of $CoNO(CO)_3$ (isoelectronic and isostructural with $Ni(CO)_4$) suggest an analogous type of behavior. Substitution reactions of CoNO-$(CO)_3$ to form $CoLNO(CO)_2$ are second order,[2] and the reagent reactivity increases with increasing polarizability of the entering ligand atom; e.g., $P(n\text{-}C_4H_9)_3$ is a much better nucleophile toward this substrate than is pyridine. For L = $As(C_6H_5)_3$, a poor reagent, a plot of rate constants vs. concentration of L is linear but has a nonzero intercept. The value of this rate constant at zero concentration of L at 25° is about tenfold smaller than that for ^{14}CO exchange with CoNO-$(CO)_3$ under the same conditions. The rate of exchange is first order, being zero order in CO. Thus, the substitution path that is zero order in L and the exchange process differ in a manner that appears to be similar to that found for the $Ni(CO)_4$ system.

Thus, many reactions of metal carbonyls, previously presumed to be dissociative reactions, should be reinvestigated in light of these results. To elucidate further the mechanism of reaction of $Ni(CO)_4$, its reaction with other reagents such as ethyl isocyanide is being studied.

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