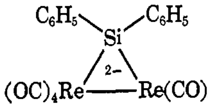
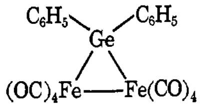
The series $[(C_6H_5)_2SiH_2Re_2(CO)_n]^+$ is the most intense in the spectrum, although all ions below the parent (*i.e.*, $0 \leq n \leq 7$) show considerable hydrogen loss. It appears that hydrogen in this compound is lost with somewhat greater ease than in $HMn_3(CO)_{10}(BH_3)_2$, in which hydrogen loss commences only after the loss of three carbonyl groups.[15]

The most convincing evidence for placing the hydrogen atoms as in Figure 1 is provided by the nmr spectrum of the dimethylsilicon analog, $(CH_3)_2SiH_2Re_2(CO)_8$.[16] *The* CH_3 *proton resonance appeared as a 1:2:1 triplet* centered at τ 8.87, with J = 1.5 Hz (CCl_4 solution). The resonance at τ 20.56 was broad, consistent with an unresolved septuplet, and upon irradiation at the high-field frequency the triplet collapsed to a singlet. The high-field protons are thus magnetically equivalent, and most probably in symmetrically equivalent positions in the $SiRe_2$ plane.[17] The magnitude of the coupling may also be compared with the value of 4.2 Hz in $(CH_3)_2SiH_2$ itself, and suggests that the high-field protons are proximate to the dimethylsilicon moiety.

Structurally, the molecule bears some relation to rhenium carbonyl, but has an eclipsed conformation and a slightly longer rhenium–rhenium bond length (3.121 *vs.* 3.02 Å[18]). From this viewpoint, each silicon–hydrogen bond functions as a two-electron donor to rhenium, effectively taking the place of a carbonyl group; the interaction could be described as a three-center, two-electron bond with the two electrons supplied by the original Si–H bond. Alternatively the molecule could be described as a protonated form of the (as yet hypothetical) anion **1**, which is isoelectronic with the known stable compound **2**.[10]



1



2

These compounds were prepared in the course of a program on photochemical reactions of metal carbonyls with silanes, some results of which have very recently been reported.[19] Hydrides other than silanes are also under investigation. It appears that in addition to their inherent interest, molecules such as those reported here will be useful in the synthesis of other compounds. Thus, $(C_6H_5)_2SiH_2Re_2(CO)_8$ is readily converted to the new dimeric hydride $[HRe(CO)_4]_2$; infrared spectra suggest that the latter has a hydrogen-bridged structure of D_{2h} symmetry. Further details will be reported when the crystal structure has been completed.[20]

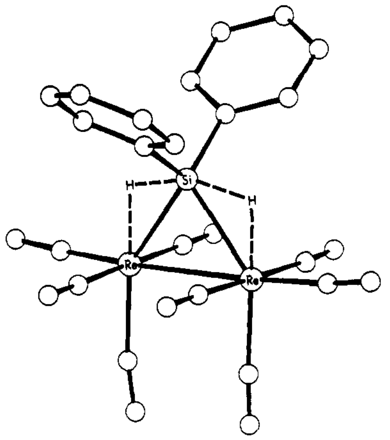


Figure 1. The molecular structure of $(C_6H_5)_2SiH_2Re_2(CO)_8$. Hydrogen atoms were not observed but are shown in the positions suggested by spectroscopic evidence (see text). Bond lengths and angles (with standard deviations) are Re–Re = 3.121 (3) Å; Re–Si = 2.51 (1) Å and 2.53 (1) Å; Re–Si–Re = 76.1 (3)°. There are no significant deviations from C_{2v} symmetry.

Acknowledgment. We thank the National Research Council of Canada for financial support.

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[14] This would not be expected for a terminally bonded hydrogen, such as $HMn(CO)_5$, where hydrogen loss is competitive with CO loss for all species: W. F. Edgell and W. M. Risen, Jr., *J. Am. Chem. Soc.*, 88, 5451 (1966).

[15] J. M. Smith, K. Mehner, and H. D. Kaesz, *ibid.*, 89, 1759 (1967).

[16] This compound was prepared in a closed vessel with intermittent release of carbon monoxide. The pale yellow, moderately air-stable crystals melt with decomposition at 115° and show infrared carbonyl bands at 2109, 2072, 2021, 2010, 1998, and 1978 cm^{-1} (cyclohexane). Satisfactory mass spectrum and microanalysis have been obtained.

[17] This argument supposes that the magnetic equivalence is neither accidental nor the result of a rapid exchange process.

[18] L. F. Dahl, E. Ishishi, and R. E. Rundle, *J. Chem. Phys.*, 26, 1750 (1957).

[19] W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **91**, 3375 (1969).

[20] Research in progress by Dr. M. J. Bennett and Miss Wendy Brooks.

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Deuteron Magnetic Relaxation Times and Molecular and Intramolecular Motion in Some Organic Liquids

Sir:

There have been several recent papers describing the application of deuteron magnetic relaxation in suitably labeled molecules to the problem of the nature of molecular and intramolecular motion in liquids.[1-4] Up to date these have (a) involved molecules where intramolecular motion is expected; (b) involved the use of extrapolated values of the quadrupole coupling constants, $e^2qQ/\hbar$; or (c) involved the use of values for the microviscosity factor,[5] f, based on other than magnetic resonance measurements in the equations

$$1/T_1 = \frac{3}{8}\left(\frac{e^2qQ}{\hbar}\right)^2 \tau_c \tag{1}$$

$$\tau_c = 0.74f\,\frac{\eta M}{\rho NKT} \tag{2}$$

by which one attempts to relate the observed relaxation rates, $1/T_1$, to calculated molecular reorientation times,

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[1] T. T. Bopp, *J. Chem. Phys.*, 47, 3621 (1967).

[2] D. E. Woessner, B. S. Snowden, Jr., and E. T. Strom, *Mol. Phys.*, 14, 265 (1968).

[3] M. D. Zeidler, *Ber. Bunsenges. Phys. Chem.*, 69, 659 (1965).

[4] D. E. Woessner, B. S. Snowden, Jr., R. A. McKay, and E. T. Strom, *J. Mag. Res.*, 1, 89 (1969).

[5] A. Gierer and K. Wirtz, *Z. Naturforsch.*, 8a, 532 (1953).

Table I. Observed and Calculated Relaxation Times for Organic Molecules and Quadrupole Coupling Constants

Compound	$T_{1,\text{obsd}}$, sec	$T_{1,\text{obsd}}/T_{1,\text{calcd}}$		$e^2qQ/\hbar$, kHz	Ref
		$f = {}^1/_6$	$f = {}^1/_{12}$		
MeBr-d_3	7.43	2.77	1.38	171 ± 4	*a*
MeI-d_3	5.84	3.86	1.93	184.3 ± 5.8	*b*
MeCN-d_3	6.90	1.96	0.98	148.3 ± 6.6	*b*
Toluene-α-d_3	5.11	5.63	2.81	165	*c*
Methylene-d_2 chloride	3.18	1.46	0.73	160 ± 3	*d*
Benzene-d_6	1.45	1.82	0.91	194 ± 4	*c*
Cyclohexane-d_{12}	1.47	2.78	1.40	174 ± 2	*c*
MeOH-d_3	6.10	2.62	1.31	165	Assumed
Acetone-d_6	4.78	2.15	1.07	165	Assumed
DMSO-d_6	0.72	1.75	0.88	165	Assumed
$(Me)_2SO_4$-d_6	2.38	1.95	0.98	165	Assumed
HOAc-d_3	1.46	1.70	0.85	165	Assumed
MeOAc-d_3	4.80	2.46	1.23	165	Assumed
Me-d_3-OAc	3.76	1.93	0.97	165	Assumed
$(OAc)_2$-d_6	2.72	3.94	1.97	165	Assumed
Aceto-d_3-phenone	1.18	4.52	2.26	165	Assumed
p-Xylene-d_6	3.46	3.96	1.93	165	Assumed
Pr-1,1-d_2-I	1.44	2.06	1.03	174	Assumed
Pr-2,2-d_2-I	1.49	2.13	1.06	174	Assumed
Pr-3,3,3-d_3-I	2.38	1.95	0.98	165	Assumed
(corrected to iodide)	1.47	1.95	0.98	165	Assumed
Toluene-d_5	1.08	1.61	0.81	194	Assumed
Cyclopentane-d_{10}	3.58	2.96	1.48	174	Assumed
Pyridine-d_5	1.11				
t-BuCl-d_9	2.32				
t-BuOH-d_9	0.26				
Aniline-d_2	0.17				
Ethylamine-d_2	2.00				
Chloroform-d_1	1.60				
Trifluoroacetic acid-d_1	0.11				

Compound	e^2qQ/h, kHz	Phase	Ref
CD_4	185	Solid	*e*
C_6D_5Br	179	Solid	*f*
p-$C_6D_4Br_2$	179	Solid	*f*
$C_{14}D_{10}$	181 ± 5	Solid	*g*
$C_{10}D_8$	193	Solid	*f*
C_2D_2	200 ± 10	Gas	*h*
CH_3C_2D	208 ± 10	Gas	*i*
FC_2D	212 ± 10	Gas	*i*
ClC_2D	225 ± 18	Gas	*i*
CD_2CO	240 ± 20	Gas	*j*
DF	340 ± 40	Gas	*k*
DOH	318.6 ± 2.4	Gas	*l*
DSH	154.7 ± 1.6	Gas	*l*
DLi	33 ± 1	Gas	*m*

[a] B. P. Dailey, Columbia University, private communication. [b] W. J. Caspary, Thesis, Columbia University, 1968. [c] J. C. Rowell, W. D. Phillips, L. R. Whelby, and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965). [d] M. P. Klein, D. Gill, and G. Kotowycz, *Chem. Phys. Letters*, **2**, 677 (1968). [e] P. Pyykko, *Ann. Univ. Turku*, **A1**, 103 (1967). [f] M. Rinne, J. Depireux, and J. Duchesne, *J. Mol. Struct.*, **1**, 178 (1967). [g] D. M. Ellis and J. L. Bjorkstam, *J. Chem. Phys.*, **46**, 4460 (1967). [h] N. F. Ramsey, *Am. Sci.*, **49**, 509 (1961). [i] V. W. Weiss and W. H. Flygare, *J. Chem. Phys.*, **45**, 8 (1966). [j] V. W. Weiss and W. H. Flygare, *ibid.*, **45**, 3475 (1966). [k] H. M. Nelson, J. A. Leavitt, M. R. Baker, and N. F. Ramsey, *Phys. Rev.*, **122**, 856 (1961). [l] P. Thaddeus, L. C. Krisher, and J. H. N. Loubser, *J. Chem. Phys.*, **40**, 257 (1964). [m] H. J. Kolker and M. Karplus, *ibid.* **36**, 960 (1962).

τ_c, or *vice versa* in terms of the viscosity, η, of the liquid, its molecular weight, M, and its density, ρ.

Since a wider range of labeled molecules is now available as well as some new, accurately determined, values of the coupling constants, it was decided to do a wider survey of deuteron relaxation times in organic liquids. Table I presents values for the observed times for a large number of previously unreported cases. In addition, it presents ratios of the observed times to those calculated with eq 1 and 2 using the coupling constants indicated, tabulated viscosities and densities, and with $f = {}^1/_6$ and ${}^1/_{12}$. The former value is that commonly accepted for pure liquids. Sections 2, 3, and 4 of Table I present T_1 values calculated on the basis of reasonable extrapolations of the accurate coupling constants. Where it is felt that no such extrapolation could be made, only the relaxation times observed are tabulated. For purposes of later discussion a short list of compounds whose coupling constants have been determined, but not their relaxation times, is also given.

The measurements were made at 31 ± 1° by adiabatic fast passage.[6] The compounds were made available by Merck Sharp and Dohme of Canada, Ltd., on a loan basis. The samples were degassed and sealed. T_1 measurements made in this study agree with those available in the literature for the same compounds at the same temperature.

(6) J. A. Glasel, *J. Sci. Instr.*, [2] **1**, 963 (1953).

The presence of intramolecular rotation results in $(T_1)_{\text{calcd}}$ on the basis of (1) and (2) being too small. That is, the mode of relaxation is less efficient than assumed in (1).[3] If molecular reorientation is anisotropic, then the reorientation time calculated from (2) is too small; that is, T_1 is too long.[4] Since cyclohexane and cyclopentane possess additional modes of angular reorientation, *e.g.*, the boat–chair interchange in the former, which have lifetimes short compared to the relaxation times observed,[7] estimates of relaxation times on the basis of (1) and (2) can be expected to be too short.

The following conclusions may be drawn from examination of Table I. The results obtained are much more understandable if a magnetic resonance microviscosity factor of $f = {}^1/_{12}$ is assumed for the pure liquids. After this correction the molecules possessing internal degrees of freedom may be picked out because their observed/calculated ratios are significantly greater than 1. Methyl cyanide, which has been one of the most popular for internal rotation studies,[1,2] has the least free rotation. The methyl groups on toluene, xylene, acetophenone, acetic anhydride, and methyl iodide are much more free. There does not appear to be internal rotation in such liquids as acetone and dimethyl sulfoxide. This is in accord with the barriers to internal rotation found for their gas phases (3.07 kcal/mole for DMSO[8] and 0.738 kcal/mole for acetone[9]) which will surely be higher in the condensed materials. The effect of internal degrees of freedom in the cycloalkanes is apparent.

It therefore appears that a modified Debye–Stokes–Einstein equation such as (2) describes magnetic resonance relaxation in a number of liquids despite the presence of association and/or anisotropic reorientation. Internal degrees of freedom exist in several molecules other than those already studied, and more complete studies on these should be of interest.

The wider variety of accurately determined deuteron quadrupole coupling constants which have recently become available make it clear that the values of these constants are remarkably invariant to substitution on an atom β to the one the deuteron is attached to in a given series of molecules. α substitution, as would be expected, has a large effect.

The following conclusions are made.

(1) A wide variety of molecules have reorientation times described by eq 1 with a microviscosity factor of ${}^1/_{12}$ rather than ${}^1/_6$. This is without recourse to other assumptions such as anisotropic rotational reorientation.

(2) Rather free internal rotation exists for methyl groups in several molecules. This is especially true in several not yet studied in detail. The presence of rapid conformational changes in the cycloalkanes effects intramolecular relaxation processes.

(3) An illustration of the utility of these relaxation techniques is provided by the various *specifically* labeled propyl halides. The results show conclusively that there is no internal rotation in the chain. Similar experiments with longer chains should prove fruitful in studies of hydrocarbon chain flexibility and conformation.

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[7] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, p 575.

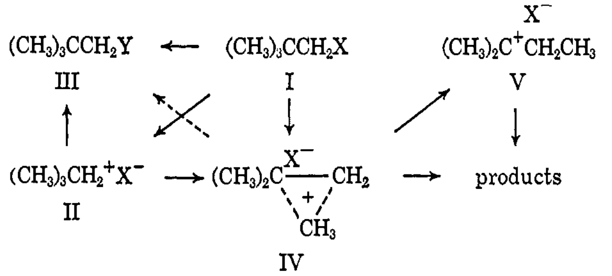
[8] H. Dreilzer and H. Dendl, *Z. Naturforsch.*, **20a**, 297 (1965).

[9] J. D. Swalen and C. C. Costain, *J. Chem. Phys.*, **31**, 1562 (1959).

The Acetolysis of Chiral 1-Adamantylcarbinyl-1′-*d* Tosylate. Evidence for a Bridged Intermediate in a Neopentyl Solvolysis

Sir:

The problem of concerted *vs.* stepwise mechanisms in the carbonium ion rearrangements of simple aliphatic substrates has remained a conundrum for many years, as exemplified by the exceptional amount of work on the neopentyl (I) and related systems.[1,2]



The deoxidation of chiral neopentyl alcohol-1-*d*,[2a] the deamination of chiral neopentylamine-1-*d*,[2d] and the ethanolysis of chiral neopentyl tosylate-1-*d*[2g] have all been shown to give rise to chiral 2-methyl-1-butene-3-*d*, formed with inversion of configuration. While these results exclude the intermediacy of a free, long-lived neopentyl cation, the possibility of a stepwise process is still not eliminated, at least for solvolysis. If the rate-determining step is ion-pair formation (I → II), and if the ion pair is so "tight" that no racemization (of deuterated substrate) occurs, conversion of chiral I to chiral V can occur without any rate enhancement due to methyl participation.[1]

Another problem, still not settled, is whether bridged structure IV is an intermediate, or merely a transition state.[2f] IV can, in principle, give rise to both primary (III) and tertiary (*via* V or directly) products, although the latter would be expected strongly to be favored. Nevertheless, it has been demonstrated recently that the use of the more nucleophilic ethanol–water solvents gives rise to appreciable (2–10%) amounts

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[1] For a review and a discussion of the pertinent literature, see J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Am. Chem. Soc.*, 88, 4475 (1966). For more recent references, see footnote 2.

[2] (a) W. A. Sanderson and H. S. Mosher, *ibid.*, **88**, 4185 (1966); (b) J. R. Owen and W. H. Saunders, Jr., *ibid.*, 88, 5809 (1966); R. L. Heidke and W. H. Saunders, Jr., *ibid.*, 88, 5816 (1966); (c) W. Kirmse and K. Horn, *Tetrahedron Letters*, 1827 (1967); (d) R. D. Guthrie, *J. Am. Chem. Soc.*, 89, 6718 (1967); (e) J. E. Nordlander and W. J. Kelly, *J. Org. Chem.*, 32, 4122 (1967); (f) G. M. Fraser and H. M. R. Hoffmann, *Chem. Commun.*, 561 (1967); (g) G. Solladie, M. Muskatirovic, and H. S. Mosher, *ibid.*, 809 (1968); (h) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Am. Chem. Soc.*, **90**, 1014 (1968); W. G. Dauben and J. L. Chitwood, *ibid.*, **90**, 6876 (1968); (i) J. J. Harper, Ph.D. Thesis, Princeton University, 1968; (k) S. H. Liggero, Ph.D. Thesis, Georgetown University, 1969; (l) C. W. Woodworth, Ph.D. Thesis, Princeton University, 1969.