a detailed explanation of this phenomenon is one of the goals of this research.

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The Resistance of Radon to Oxidation in Aqueous Solution[1]

Sir:

Haseltine and Moser[2] have reported the oxidation of radon in aqueous solution. We have recently attempted to duplicate their results, and on the basis of more than 60 experiments we have become convinced that their conclusions are incorrect.

In their most convincing result, Haseltine and Moser found that when a solution 10^{-7} *M* in $^{226}RaBr_2$ and 0.1 *M* in $K_2S_2O_8$ was allowed to stand for 23 days, most of the ^{222}Rn formed could not be extracted into hexane and could not be volatilized by bubbling a gas through the solution.

We have repeated this experiment using $^{226}RaCl_2$ solutions, but otherwise duplicating the conditions of Haseltine and Moser. We found that less than 6% of the radon remained in the 23-day old persulfate solution after argon had been bubbled through it for 3 hr, or after it had been extracted with an equal volume of hexane. On the other hand, after the solution had stood for 38–39 days, 80% of the radon could not be volatilized by argon bubbling, and two-thirds of it did not extract into an equal volume of hexane. This radon could, however, be removed from solution by centrifuging in a clinical centrifuge. After the supernatant solution was withdrawn, the radon activity in the residue increased with time. This indicated that the residue contained radium, with which the radon had not yet reached equilibrium.

We have attempted to oxidize radon in the same way with the other reagents tried by Haseltine and Moser, and also with ozone and with sodium perxenate. In no case was a solution obtained from which the radon could not be removed either by bubbling in argon or by centrifuging; and whenever the radon was removed by centrifugation, it was accompanied by radium in excess of the equilibrium amount. It is noteworthy that even from some $RaCl_2$ solutions containing no other reagents, significant portions of the radon could not be volatilized, but could be removed by centrifugation.

We conclude from these studies that the phenomena observed by Haseltine and Moser do not result from oxidation of radon. They seem instead to be brought about by the precipitation of some or all of the radium by reagents or impurities in the solutions. (The sulfate that gradually builds up in persulfate solutions is one likely cause of such precipitation.) The radon that forms within the precipitate is mechanically trapped and will neither extract into hexane nor volatilize in a gas stream.

We have found no evidence for the existence of radon compounds in aqueous solution, and we hope that others will undertake to verify our conclusions.

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) M. W. Haseltine and H. C. Moser, *J. Am. Chem. Soc.*, **89**, 2497 (1967).

Rapid Time Scale for Hydrogen-Atom Abstraction by Recoil Tritium Atoms. Nonequilibrium Allyl Radicals from Propylene

Sir:

We have measured the HT yield from the recoil tritium abstraction reaction with the CH_3 group of propylene, as in (1), and have compared it to the well-established correlation of hydrocarbon bond dissociation energies with such hydrogen abstraction yields.[1–6] The discrepancy between this apparent value for the allyl–H bond dissociation energy (93 kcal/mole) and the measured values by other well-established techniques (87.8 kcal/mole)[7] leads us to the conclusion that the equilibrium bond dissociation energy is not appropriate for such a comparison in this particular situation. We believe that the lower yield characteristic of a stronger bond reflects the fact that the transfer of the hydrogen atom from C_3H_5–H bonding to the T–H bonding is completed while the bond lengths (and perhaps the angles) of the C_3H_5 residue still differ substantially from those of an allyl radical in its equilibrium configuration.

$$T^* + CH_3{-}CH{=}CH_2 \longrightarrow HT + CH_2{-}CH{=}CH_2 \qquad (1)$$

The largest geometrical differences between propylene and allyl involve the C–C distances and the C–C–C bond angle. Failure to attain the equilibrium allylic configuration during H-atom transfer is thus essentially equivalent to very high vibrational excitation of the C–C stretching and C–C–C bending vibrations of the allyl radical, and represents relaxation energy not yet totally available for "loosening" of the C–H bond at the time of atom transfer. Since the C_1–C_2 and C_2–C_3 bond distances are 1.336 and 1.501 Å, respectively, in propylene,[8] and about 1.40–1.44 Å in the equilibrium allyl radical,[9] the chief geometrical deformation in terms of energy involves deviations in C–C bond distances as much as 0.1 Å.

We conclude that the time scale for the hydrogen-abstraction reaction is definitely shorter than that required for complete adjustment of geometric relationships to those of the thermally equilibrated allyl radical. By assuming that the time required for 0.1-Å adjust-

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(1) W. Breckenridge, J. W. Root, and F. S. Rowland, *J. Chem. Phys.*, **39**, 2374 (1964).

(2) J. W. Root and F. S. Rowland, *J. Phys. Chem.*, **68**, 1226 (1964).

(3) J. W. Root, W. Breckenridge, and F. S. Rowland, *J. Chem. Phys.*, **43**, 3694 (1965).

(4) R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965).

(5) E. Tachikawa, Ph.D. Thesis, University of California at Irvine, 1967; E. Tachikawa and F. S. Rowland, *J. Am. Chem. Soc.*, in press.

(6) All HT yields are expressed as yields per C–H bond under equivalent conditions of exposure to energetic tritium atoms.

(7) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5420 (1964); D. M. Golden, A. S. Rodgers, and S. W. Benson, *ibid.*, **88**, 3196 (1966).

(8) D. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).

(9) C. L. Currie and D. A. Ramsay, *ibid.*, **45**, 488 (1966).

Table I. Abstraction Yields from Recoil Tritium Reactions with Propylene in Excess Perfluorocyclobutene

	Parent molecule					Approx average
	$CH_3CH{=}CH_2$	$CH_3CD{=}CD_2$		$CD_3CH{=}CD_2$	$CD_3CD{=}CD_2$	
Relative yields[a]						
Total molecule						
HT	9300	6490	6170	1200	...	
DT	...	1880	1870	5630	7200	
Per bond						
CH_3	1550 (av)	2160	2060	...	...	2100
CD_3	...	...	...	1130 (av)	1200 (av)	
CH	(av)	...	...	1200	...	1200
CD	...	(av)	(av)	...	(av)	
CH_2	(av)	...	...	...	...	800
CD_2	...	630 (av)	620 (av)	(av)	(av)	

[a] HT from CH_4 = 2500; per C–H = 625.

ments in C–C bond distances would be roughly comparable to the period of a C–C stretching vibration ($\sim$1200 cm^{-1} or 3×10^{-14} sec), the time scale for the typical abstraction reaction is indicated as not longer than about $2\text{–}5 \times 10^{-14}$ sec. For comparison of the times and distances involved, one can recall that tritium atoms of 1 and 50 eV have velocities of 8×10^{13} Å/sec and 6×10^{14} Å/sec, respectively, corresponding to translational motions of 2 and 20 Å in a period of 3×10^{-14} sec.

The additional question can be asked whether there is sufficient time for *any* appreciable relaxation of the geometrical structure of C_3H_5 toward that of the allyl radical during reaction 1; for example, a stripping mechanism[4] involving hydrogen-atom transfer during the grazing passage of a 50-eV tritium atom would require a time scale of about 2×10^{-15} sec. The correlation of bond dissociation energies with HT yield has, of course, been established through study of the recoil abstraction reaction, presumably on the same time scale, with a number of other molecules, each of which may *also* require some geometrical adjustments of the residual radical during or after the hydrogen atom transfer step, *e.g.*, planar CH_3 from T* + CH_4. The success of the correlation indicates that these factors are either negligible, or cancel out, in these other cases for which the possible residual excitation energies are so much smaller.[3,5] We suggest that the higher abstraction yields found from CH_3 in propylene *vs.* that from CH_3 in ethane, propane, or neopentane indicate that some adjustment in geometrical structure has already occurred in the C–C bond distances at the time of reaction, and partially reflect the extra stability of the residual radical left after completion of the reaction. By inference, we conclude that the time scale of the abstraction reaction is usually $\lesssim 10^{-14}$ sec, and place the median energy of the hot abstraction reaction in the low electron volt range, and not in the range of either tenths or tens of electron volts.

The recoil tritium reactions were carried out with a variety of isotopic propylene molecules as targets and utilized radio gas chromatographic analysis of the separated HT and DT peaks to identify the yields from particular positions, including that of the CH_3 group. These data are summarized in Table I, and can be compared with the following values for relative HT yields under equivalent conditions:[5,6,10] CH_4, 625, 104.0 kcal/mole;[11] *neo*-C_5H_{12}, 966, 99.3 kcal/mole; C_2H_6, 1150, 98.0 kcal/mole; *c*-C_5H_{10}, 2130, 92.9 kcal/mole; CH_2Br_2, 2350; $CHCl_3$, 9100. The various isotopic propylene molecules give consistent results, and the relative HT yield from CH_3 in propylene is approximately equal to that for C–H in cyclopentane, nominally corresponding to a bond dissociation energy of $\sim$93 kcal/mole.

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[10] Perfluorocyclobutene was used extensively in ref 5 as the major component required to establish equivalent conditions of tritium flux for different RH molecules; comparable results were also obtained for these additional systems: perfluorobutadiene, argon, nitrogen, C_2D_4.

[11] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

[12] This research was supported by A.E.C. Contract No. AT-(11-1)-34, Agreement No. 126.

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Magnetic and Spectral Properties of $[Fe(en)_3]Cl_3$

Sir:

Relatively little information is available on the d–d spectra of low-spin Fe(III) complexes. This is due primarily to the fact that complexes of ligands strong enough to cause spin pairing such as CN$^-$, phen, bipy, and terpy have relatively intense charge transfer and/or ligand bands in the visible which obscure the d–d bands. Naiman[1] has interpreted the spectrum of $Fe(CN)_6{}^{3-}$ and obtained values of 10*Dq* and the Racah parameter *B* of 35,000 and 720 cm^{-1}, respectively.

We have recently prepared[2] $[Fe(en)_3]Cl_3$[3] which is low-spin and is sufficiently free of charge-transfer bands to allow a reasonably quantitative interpretation of the very rich d–d spectrum. The reflectance spectra[4] at 80 and 290° are shown in Figure 1. As can be seen, the

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[1] C. S. Naiman, *J. Chem. Phys.*, **35**, 323 (1961).

[2] The compound was prepared by adding slowly and with stirring a stoichiometric amount of 98% en in absolute ethanol to a solution of anhydrous iron(III) chloride also dissolved in absolute ethanol. The flesh-colored solid was filtered, washed with ether, and dried in a vacuum. The preparation, filtration, and drying were carried out in a closed system under nitrogen. The dry solid is stable for months in a desiccator. *Anal.* Calcd for $FeC_6N_6H_{24}Cl_3$: C, 21.03; H, 7.08; N, 24.54. Found: C, 21.26; H, 6.79; N, 24.57.

[3] That the compound is actually as represented, that is, one having three chelated en groups, is indicated by several lines of evidence. The X-ray powder pattern is essentially identical with that of $[Cr(en)_3]Cl_3$ which in turn was characterized by its absorption spectrum. Further, molar conductivity measurements in absolute methanol give values of 163 compared to 187 for $Cr(NO_3)_3 \cdot 9H_2O$.

[4] Spectra were also obtained in methanol solution and as mulls in Kel-F grease. From the solution spectra it can be concluded that the maximum value of the molar extinction coefficient for any of the bands assigned is 50. The precise values cannot be determined because of overlapping of the bands. Resolution in these media was not as good as in the reflectance although there seems to be general agreement of the more intense bands.