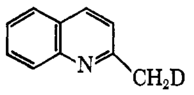
(but from a far more reactive $-CH_2OH$) was made on the basis of deuterium isotope studies.

Irradiation[2] of VII yielded VIII and formaldehyde. By nmr integration and mass spectrometry no detectable III was present and the formaldehyde was free of CHDO. Thus, the alcoholic hydrogen was specifically



VIII

transferred. Again, the mass spectrum of VII correlated perfectly, with the base peak appearing at *m/e* 144 instead of *m/e* 143 as in the case of IV. As further confirmation of the close parallel of these reactions with type II cleavage and the McLafferty rearrangement we found that compound IX was completely stable to irradiation under the same conditions, while its electron impact fragmentation gave a base peak at *m/e* 155 (vinylquinoline). In IX a six-membered transition state for H abstraction is not possible.

Studies on the excited state(s) involved in these photoreactions are currently under way.

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Variations with Bond Types of the Yields for Deuterium-Atom Abstraction by 2.8-eV Tritium Atoms

Sir:

The reaction yields from the abstraction of hydrogen by energetic tritium atoms from nuclear recoil, as in (1), vary widely with C–H bond type and exhibit a good correlation between higher HT yield and lower bond dissociation energy of the C–H bond for a series of cyclanes and alkanes.[1-4] Subsequent experiments

$$T^* + RH \longrightarrow HT + R \qquad (1)$$

have confirmed the general concept of substantial variations in HT yield with C–H bond type, while demonstrating that the bond dissociation energy correlation must be modified in some cases by allowances for the internal excitation of the residual radical, R.[5,6] Explanations of two general types have been offered to account for the observed sensitivity of HT yield to the nature of the C–H bond, differing most critically in their estimates of the kinetic energy of the reacting tritium atom. One proposal invokes an "energy cut-off" model,[2,3] correlating the yield behavior with the known lower energy thresholds for abstraction from weaker C–H bonds.[7] An alternate mechanistic proposal is the high-energy, "stripping" model,[8,9] which hypothesizes that (a) the hydrogen-abstraction process occurs largely through grazing collisions at relatively high tritium atom energies, and (b) the weaker C–H bonds permit higher yields for such encounters. The energy arguments in support of each model have necessarily been indirect in previous experiments utilizing tritium from nuclear recoil, since all of these atoms are formed with 192,000-eV kinetic energy, and a fraction of them become completely thermalized without reaction, thereby ensuring that all possible energies of reaction are sampled in the experiment.

We have now carried out a series of abstraction reactions from deuterated compounds[10] with 2.8-eV tritium atoms from the 1849-Å photolysis of TBr,[11] and have observed a characteristic, strong dependence of abstraction yield upon the nature of the attacked C–D bond, as shown in Table I. The yields have been expressed as $(DT)_C{}^{2.8}$, the relative yield per C–D bond, from the abstraction of 2.8-eV atoms in excess CH_4.

Table I. Relative Yields of DT from Reactions of 2.8-eV Tritium Atoms with RD

	Relative yields[a,b]	
Compound	$(DT)_C{}^{2.8}$	$(HT)_F{}^{\infty}$, ref 3
CD_4	(1.0)	(1.00)
neo-C_5D_{12}	1.7	1.54 ± 0.03
C_2D_6	2.4	1.84 ± 0.05
c-C_4D_8	2.8	2.77 ± 0.10
C_3D_8	3.4	1.67 ± 0.10
CDF_3	1.3	1.34 ± 0.04
CD_3F	2.7	1.70 ± 0.05

[a] Yields are given as values of $(DT)_C{}^{2.8}$, the relative yield per bond *vs.* yield from C–D of CD_4, as measured in bulk CH_4 with 2.8-eV T atoms: $CH_4/RD \sim 10$; Br_2, 2–7%. [b] The values of $(HT)_F{}^{\infty}$ are the relative yields from RH, as measured in bulk perfluorocyclobutene with 192,000-eV T atoms.

Our measurements have been carried out with CH_4–RD mixtures in a mole ratio of ~10 to ensure that the bulk of the nonreactive collisions have similar energy-loss patterns for all mixtures. The mixtures also contained 2–7% Br_2 as scavenger. This technique is quite similar to that used in the nuclear recoil experiments and has been adopted because of the nearly complete absence of quantitative experimental information concerning energy losses in nonreactive collisions in the 1–20-eV range. Preliminary results indicate that the value of $(DT)_C{}^{2.8}$ is slightly dependent upon Br_2 concentration (~10%), in the pattern of experiments with CH_4,[11] and varies less than 10% with varying mole fractions of CH_4 and RD in the mixture. The variations observed for tritium atoms from nuclear recoil, listed for comparison in Table I, are similar in magnitude to those from the photochemical experiments. The values of $(DT)_C{}^{2.8}$ and $(HT)_F{}^{\infty}$ are not entirely parallel, with the variations for CD_3F and

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[10] Deuterated compounds are technically somewhat easier to use without ambiguity in the photochemical experiments. Much less extensive work has established that the abstraction of deuterium from C–D by tritium atoms from nuclear recoil fits readily into a pattern of variation quite similar to that found for C–H.[2-4]

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C_3D_8 being noticeably different from, for example, *neo*-C_5D_{12} and *c*-C_4D_8. The higher value for CD_3F than CD_4 in both cases is noteworthy since this reverses the trend found in alkanes of lower yield with higher bond dissociation energy; the reversal has been attributed in the nuclear recoil case to the difference in structure between planar CH_3 and nonplanar CF_3 groups, and consequent accompanying differences in residual excitation following the fast abstraction reaction.[6]

Absolute measurements of yield are not feasible in our experiment.[11] However, hot yields (presumably mostly of the abstraction product[11]) as high as 31% have been found for 3-eV H* or D* reactions with hydrocarbons,[12–15] while abstraction yields of 20–40% are found in experiments with hot tritium atoms from nuclear recoil.[8] Detailed quantitative comparison of the two kinds of experiments would require knowledge of the energy losses in the nonreactive collisions of tritium with each molecule of the mixture over the whole possible energy range. Within the semiquantitative range of present estimates, the magnitude of the DT yield variations in the photochemical experiments is sufficient to account for much of the corresponding variation found in nuclear recoil experiments. The photochemical experiments imply that low energy (<3 eV) abstraction reactions comprise an appreciable part of the observed nuclear recoil abstraction yields, and are consistent with the "energy cut-off" model for such reactions.

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Cation-Induced Linkage Isomerism of the Thiocyanatopentacyanocobaltate(III) Complex

Sir:

The mode of bonding of the ambidentate ligand thiocyanate to transition metals has been shown to be subject to a variety of influences; these include the nature of the metal,[1–3] the steric and electronic characteristics of other ligands in the coordination sphere,[1,4–6] and the nature of the solvent.[7] In a recent report a noncoordinated anion was shown to influence the mode of bonding in $[Pd(Et_4dien)NCS]^+$.[8] We now wish to report that for the complex $Co(CN)_5SCN^{3-}$ the nature of the countercation determines which of the two linkage isomers is the more stable in solid materials.

The complex $K_3[Co(CN)_5SCN]$ was first prepared several years ago and shown to be stable to isomerization in the solid state.[9] More recently, the linkage isomer $K_3[Co(CN)_5NCS]$ has been reported.[10] We have converted each of these compounds to a tetra-*n*-butylammonium salt by extracting an aqueous solution of complex with a solution of $[(n\text{-}C_4H_9)_4N]Cl$ in methylene chloride, evaporating the organic layer, and recrystallizing the residue from methylene chloride–ether. We have also converted $K_3[Co(CN)_5SCN]$ to a tetra-*n*-butylammonium salt by preparing the acid $H_3[Co(CN)_5SCN]$, titrating it to neutral pH with $[(n\text{-}C_4H_9)_4N]OH$, and removing the water under reduced pressure.

The crystalline $(n\text{-}C_4H_9)_4N^+$ salts prepared by the three pathways have identical electronic absorption spectra in aqueous solution (Table I) and identical infrared spectra in the C≡N stretching region (2140 cm^{-1}, s, br; 2113 cm^{-1}, vs) and may therefore be presumed to contain the same anionic linkage isomer. An unambiguous assignment of the mode of bonding in this compound is complicated by the presence of absorptions of $(n\text{-}C_4H_9)_4N^+$ in the region of the infrared spectrum where the C–S stretching band is expected and absorptions of the $[Co^{III}(CN)_5]$ unit in the regions of the other thiocyanate fundamentals. However, a potassium salt, prepared by metathesis of the compound with KNCS in ethanol, shows an infrared absorption at 812 cm^{-1} assignable[1,2] to the C–S stretching mode of a nitrogen-bound thiocyanate; this potassium salt must then be the $K_3[Co(CN)_5NCS]$ isomer. The electronic spectra of $K_3[Co(CN)_5NCS]$ and the tetra-*n*-butylammonium salt are essentially the same and both are considerably different from the spectrum of $K_3[Co(CN)_5SCN]$. Thus the crystalline tetra-*n*-butylammonium salt must contain exclusively the isothiocyanatopentacyanocobaltate(III) anion, $Co(CN)_5NCS^{3-}$.[11]

Table I. Electronic Spectra of $Co(CN)_5NCS^{3-}$ and $Co(CN_5)SCN^{3-}$ in Aqueous Solution

Compound	λ_{max}, nm	ϵ_{max}
$[(n\text{-}C_4H_9)_4N]_3[Co(CN)_5NCS]$	363	500
	265	2,350
	202	28,000
$K_3[Co(CN)_5NCS]$	363	447
	265	2,360
	203	24,000
$K_3[Co(CN)_5SCN]$	378	191
	265	17,100
	227	4,300
	200	16,700
$K_3[Co(CN)_5CNS]^a$	363	260
	263	13,800

[a] Spectrum of the compound reported in ref 10. This may be interpreted as a spectrum of a mixture of about 70% $K_3[Co(CN)_5SCN]$ and about 30% $K_3[Co(CN)_5NCS]$.

In aqueous solution the linkage isomerization of either $Co(CN)_5NCS^{3-}$ or $Co(CN)_5SCN^{3-}$ is a relatively

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