mol % of the consumed 7.[6] Quadricyclane was formed no more than 1 mol % of the consumed 7, showing that the rearrangement of 4 to 5 is quite fast. Judging from the unsuccessful trial to trap 4, we can estimate the rate of the rearrangement to be faster than the cyclization of hex-5-en-1-yl radical to cyclopentylmethyl radical ($\sim 10^5$ s^{-1} at 40 °C)[7,8] and to be of similar rate to or even faster than the interconversion between nortricyclyl and norborn-5-en-2-yl radicals ($\sim 10^8$ s^{-1}).[8-10]

The rearrangement of 4 to 5 was studied also with ESR technique. Photolysis of an ethane solution of a mixture of 3-bromoquadricyclane,[11] triethylsilane, and di-*tert*-butyl peroxide or of a mixture of quadricyclane and the peroxide at −146 °C in an ESR cavity gave a spectrum consisting of three sets of 1:2:1 triplets (19.9_2, 14.0_1, and 1.74 G) split into doublets of 2.71 G at g = 2.00267, which is identical with the spectrum of 5[12] generated by photolysis of a mixture of di-*tert*-butyl peroxide and bicyclo[3.2.0]hepta-2,6-diene.[4b] An ESR spectrum of 6 was observed during photolysis of an ethane or cyclopropane solution of a mixture of 7-bromonorbornadiene, triethylsilane, and di-*tert*-butyl peroxide.[13] There was no indication of the formation of 5 in the spectra observed in the examined temperature range between −60 and −146 °C. If 4 rearranged to 5 via 6, as one might conceive on the basis of chemistry of cationic analogues, we should have observed 5, not 6, in the latter ESR experiment, but this is not the case.

When 7-bromonorbornadiene[14] (0.22 mmol) was reduced with the stannane (0.13 mmol) in *n*-hexane (0.15 mL) in the presence of di-*tert*-butyl peroxide (0.004 mmol) at 130 °C for 15 min,[15] norbornadiene was formed in 72% yield based on the stannane and 8 was not detected (<1 mol % of the stannane). This result shows that 6 does not rearrange to 5 at higher temperatures either.

These results of present product and ESR studies indicate that 4 rearranges to 5 with a fast rate and that 6 is not involved in this rearrangement. The predominant formation of bicyclo[3.2.0]heptadiene derivatives by the rearrangement of 4 to 5 may provide a diagnostic tool for differentiating homolytic processes from those involving carbonium ion intermediates; the latter give norbornadiene and/or quadricyclane derivatives.[3b,16]

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ment. However, 4 rearranged to 5 before the silane traps 4 in a similar reaction condition (vide infra). (b) Y. Sugiyama, T. Kawamura, and T. Yonezawa, *Chem. Lett.*, 639 (1978).
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Infrared Laser Photochemistry of Matrix-Isolated Molecules

Sir:

Two groups have reported studies of infrared laser induced photochemistry of matrix-isolated species. Turner et al.[1] have examined rearrangements of isotopically labeled carbonyl fragments induced by radiation from a carbon monoxide laser in the 1900-cm^{-1} region. These authors have concluded[1b] that "a single molecule requires absorption of only one photon to undergo isomerization". Ambartzumian et al.[2] claim to have observed selective dissociation of ^{32}SF$_6$ in argon matrices using a carbon dioxide laser operating in the 940-cm^{-1} region. They estimate that each molecule absorbs energy corresponding to about 150 quanta of CO$_2$ laser radiation.[2b] Some aspects of their reported conclusions appeared unusual to us and we attempted to reproduce their results and extend work in this field.

We were surprised that no dissociated products were detected using infrared spectroscopy,[2b] since for the species that may be produced (SF$_4$, S$_2$F$_{10}$, and SF$_5$·) vibrational data are available.[3-5] A reported decrease in absorption due to ^{32}SF$_6$ from ~95 to ~55%[2b] would be expected to yield photoproducts having substantial absorbances.

We have carried out a series of experiments involving CO$_2$ laser irradiation of various matrix-isolated molecules and have not observed any evidence for dissociation or reaction in this medium. Table I shows some of the species studied, the vibrational modes excited, and the laser wavenumbers employed. Matrix ratios were in the range 100:1 to 40 000:1, and slow spray-on techniques were used. Our observations of the effects of irradiation are that no spectroscopic or visual effects were observed (a) for irradiation of pure argon matrices or (b) when the exciting frequency was more than 10 cm^{-1} away from an absorption band. Irradiation of the matrix at a guest absorption frequency (or at up to 5 cm^{-1} to lower wavenumber) with low energy density (0.4 J cm^{-2}) causes "fogging" of the previously glassy matrices, and at higher densities (40 J cm^{-2}) causes matrix destruction with complete evaporation. Prolonged photolyses have led to fracturing of the cesium iodide substrate. We are led to the conclusion that the spectra presented by Ambartzumian et al. show no conclusive evidence of dissociative photochemistry but may simply be interpreted in terms of differential evaporation of ^{32}SF$_6$ from the matrices.

Table I

compd[a]	laser line	frequency	mode	reported IR gas phase photolysis
SF_6[b]	P(20) 001–100	944.2	ν_3	c
	P(26)	938.7		
N_2F_4[d]	P(20) 001–100	944.2	ν_8[e]	f
NF_3[g]	P(38) 001–020	1029.4	ν_1	
COS[h]	P(20) 001–020	1046.8	$2\nu_2$	
O_3[i]	P(30) 001–020	1037.4	ν_1	

[a] Matrix materials used were Ar, 99.9998% (Matheson); N_2, 99.997% (Linde); and NO, 99.0% (Matheson). [b] Matheson, 99.8%. [c] R. V. Ambartzumian, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, *JETP Lett.*, **21**, 171 (1975); J. L. Lyman, R. J. Jensen, J. P. Rink, C. P. Robinson, and S. D. Rockwood, *Appl. Phys. Lett.*, **27**, 87 (1975). [d] Air Products, 98%. [e] Gauche isomer: J. R. Durig, B. H. Gimarc, and J. D. Odom in "Vibrational Spectra and Structure", Vol. 2, J. R. Durig, Ed., Marcel Dekker, New York, 1975, p 35. [f] J. L. Lyman and R. J. Jensen, *Chem. Phys. Lett.*, **13**, 421 (1972). [g] Air Products, 98%. [h] Matheson, 97.5%. [i] Prepared in situ using microwave discharge. See L. Brewer and J. L. Wang, *J. Chem. Phys.*, **56**, 759 (1972).

After submitting this paper, we have learned that Davies et al.[6] have also observed *apparent* isotopic enrichment when SF_6, isolated in solid CO or Ar, is irradiated with a pulsed CO_2 laser. The authors attribute this result to a spectroscopic artefact caused by the ablation of the matrix.[6]

The vacuum, cryogenic and spectroscopic equipment has been described previously.[7] A Lumonics TEA 103-2 CO_2 laser was operated in the 10.6-μ region with an energy of 1–2 J per pulse. Output modes were monitored using an Optical Engineering Model 10R spectrum analyzer.

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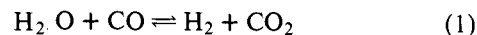
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Applications of the Water-Gas Shift Reaction. 2.
Catalytic Exchange of Deuterium for
Hydrogen at Saturated Carbon

Sir:

The homogeneous catalysis of the water-gas shift reaction (WGSR) (eq 1) by metal complexes of groups 6 and 8 has been

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad (1)$$

demonstrated by a number of research groups.[1-5] Recently, catalyst solutions similar to those used for catalyzing the WGSR have been used successfully to catalyze hydroformylation and hydrohydroxymethylation, where H_2O serves as a source of hydrogen.[5]

All of the reported catalyst systems, with the exception of Eisenberg's WGSR catalyst solution,[3] require a basic medium to effect catalytic action. In our previous work,[2,5] we have used aqueous alcoholic solutions of group 8 metal carbonyl complexes made basic with KOH. In an attempt to simplify our reaction system, we substituted triethylamine (Et_3N) for KOH as base, and for alcohol as solvent. This substitution led to the discovery that Et_3N in the presence of D_2O, CO, and $Rh_6(CO)_{16}$ at 150 °C undergoes an unusual catalytic exchange of deuterium for hydrogen.[6]

When 6 mL (0.043 mol) of Et_3N (distilled from CaH_2), 2 mL (0.055 mol) of D_2O (99+% D) and 106 mg (1×10^{-4} mol) of $Rh_6(CO)_{16}$ are heated with stirring under 800 psi of CO for 20 h at 150 °C, the recovered Et_3N contains 0.5% Et_3N-d_1, 1.4% Et_3N-d_2, 5.6% Et_3N-d_3, and 9.5% Et_3N-d_4, as determined by both 11-eV electron impact and water chemical ionization mass spectrometry.[7,8] A total of 23% of all deuterium initially present as D_2O has been incorporated into the triethylamine,[9] so the remaining water may contain substantial quantities of HDO. In order to determine the initial distribution of deuterated Et_3N produced, aliquots of the reaction mixture taken at 5, 10, and 15 h were analyzed and the product distributions extrapolated back to zero time, when the D_2O still contained 99+% D. The initial product distribution thus obtained was 2.8% Et_3N-d_1, 7.7% Et_3N-d_2, 19.0% Et_3N-d_3, and 70.4% Et_3N-d_4.

The 11-eV mass spectrum of unlabeled Et_3N shows a fragment at m/e 86 corresponding to loss of methyl radical from one of the ethyl groups. In the 20-h reaction product spectrum, this fragment ion is 85.3% d_0, 3.6% d_1, 0.8% d_2, 3.4% d_3, and 6.9% d_4. This distribution of deuterium in the fragment ion can only be accounted for if *three of the four hydrogens exchanged in Et_3N are on the same methyl group*. The distribution calculated on this basis from the distribution of labeled Et_3N given above is 85.4% d_0, 3.5% d_1, 0.9% d_2, 3.7% d_3, and 6.4% d_4. In the calculation, it was assumed that the probability of losing the labeled methyl group was 1/3 (no secondary deuterium isotope effect) and that all of the deuteriums in the Et_3N-d_1, -d_2, and -d_3 were on the methyl group. (The latter assumption is of course not completely correct and results in the predicted amount of d_0 being too high, while the predicted amount of d_1 is too low by the same amount.)

The remaining deuterium to be assigned is the fourth one of the d_4-labeled material, which must be on one of the methylene groups. A similar analysis of mass spectral data, obtained at 70 ev, for m/e 62 (M-d_4 minus -CH_3 minus C_2H_4) shows this methylene to be the one adjacent to the labeled methyl; i.e., the d_4 molecule contains -CDH-CD_3.[10]

Deuterium NMR supports these conclusions, giving peaks at δ 0.95 (4 ± 0.4 D, -CD_3), 2.40 (1 D, -CDH-).[11]

The IR of the aqueous portion of the reaction solution gives metal carbonyl stretching vibrations at ν_{CO} 2095 (vw), 2035 (vs), 1787 (m) cm^{-1}, which are reminiscent of those reported by Chini for $Rh_6(CO)_{15}X^-$ (X = -H, -CN, -Cl, -Br, -I, -CO_2R, -CONHR).[12] We have isolated a brown material with these stretching vibrations and are attempting to purify the complex at present.

A mechanism that may explain the above results is shown in Scheme I. The mechanism requires initial coordination of the nitrogen lone pair to metal (1) followed by metal insertion into the adjacent carbon–hydrogen bond to form a coordinated nitrogen ylide (1) of the type observed recently by Kaesz et al.[13]