

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 ₂ F ₄ ^d	P(20) 001-100	944.2	ν_8 ^e	f
	NF ₃ ^g	P(38) 001-020	1029.4	
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); N₂, 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 SF₆, isolated in solid CO or Ar, is irradiated with a pulsed CO₂ 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 CO₂ 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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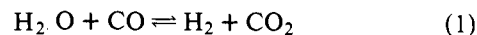
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Applications of the Water-Gas Shift Reaction. 2. Catalytic Exchange of Deuterium for Hydrogen at Saturated Carbon

Sir:

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



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 H₂O 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 (Et₃N) for KOH as base, and for alcohol as solvent. This substitution led to the discovery that Et₃N in the presence of D₂O, CO, and Rh₆(CO)₁₆ at 150 °C undergoes an unusual catalytic exchange of deuterium for hydrogen.⁶

When 6 mL (0.043 mol) of Et₃N (distilled from CaH₂), 2 mL (0.055 mol) of D₂O (99+% D) and 106 mg (1 × 10⁻⁴ mol) of Rh₆(CO)₁₆ are heated with stirring under 800 psi of CO for 20 h at 150 °C, the recovered Et₃N contains 0.5% Et₃N-d₁, 1.4% Et₃N-d₂, 5.6% Et₃N-d₃, and 9.5% Et₃N-d₄, 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 D₂O 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 Et₃N 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 D₂O still contained 99+% D. The initial product distribution thus obtained was 2.8% Et₃N-d₁, 7.7% Et₃N-d₂, 19.0% Et₃N-d₃, and 70.4% Et₃N-d₄.

The 11-eV mass spectrum of unlabeled Et₃N 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 Et₃N are on the same methyl group*. The distribution calculated on this basis from the distribution of labeled Et₃N 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 Et₃N-d₁, -d₂, and -d₃ 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.)

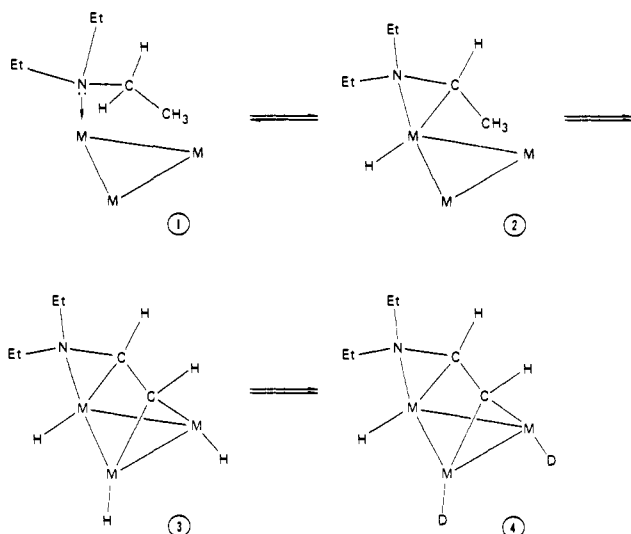
The remaining deuterium to be assigned is the fourth one of the *d*₄-labeled material, which must be on one of the methylene groups. A similar analysis of mass spectral data, obtained at 70 eV, for *m/e* 62 (M-d₄ minus -CH₃ minus C₂H₄) shows this methylene to be the one adjacent to the labeled methyl; i.e., the *d*₄ molecule contains -CDH-CD₃.¹⁰

Deuterium NMR supports these conclusions, giving peaks at δ 0.95 (4 ± 0.4 D, -CD₃), 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 Rh₆(CO)₁₅X⁻ (X = -H, -CN, -Cl, -Br, -I, -CO₂R, -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

Scheme I



and Deeming and Yin.¹⁴ The methyl group now lies above the plane of the metal triangle and can react with the remaining two metals to produce the insertion product (3).¹⁵ If exchange of deuterium for hydrogen (3 → 4) is faster at the two metals not bound to nitrogen and the reactions 3 → 2 and 2 → 3 are faster than 2 → 1, then the major products must be Et₂NCHDCD₃ and Et₂NCH₂CD₃.

To test this proposed mechanism, we substituted 6.0 mL of (CH₃CH₂CH₂)₃N ((npr)₃N) for Et₃N with the expectation that (npr)₂N-CHDCD₂CH₃ and (npr)₂NCH₂CD₂CH₃ would be the major products. After the compound was heated for 20 h under identical conditions, 1.6% *d*₃ as (npr)₂CHDCD₂CH₃ and 0.7% *d*₂ as (npr)₂NCH₂CD₂CH₃ were the only significant deuterated products found.¹⁶ The lower exchange rate as compared with Et₃N is probably the result of increased steric interactions.

This reaction represents one of the few homogeneous catalytic reactions wherein activation of hydrogen at saturated carbon occurs.^{6,17} Recently Murahashi et al.¹⁸ have reported the catalytic activation of tertiary alkyl amines by heterogeneous platinum catalysts wherein deuterium exchange experiments indicate metal insertion into the α-carbon-hydrogen bond. This suggests that the present homogeneous catalyst system could be used advantageously for modeling heterogeneous catalytic reactions such as that reported by Murahashi. Moreover, since the experimental data implicates the need for three metal centers (a cluster) during catalysis, then the work described here constitutes validation for Muetterties proposal that homogeneous metal cluster catalysis can be used to model heterogeneous catalytic reactions.¹⁹

The studies of Deeming^{14,15} and Kaesz¹³ indicate that this type of homogeneous catalysis reaction may be common to a number of transition metal carbonyl complexes, especially those of group 8.

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- (7) Electron impact mass spectra were obtained with an LKB 9000 mass spectrometer equipped with a gas chromatograph. Chemical ionization mass spectra were obtained on a modified Du Pont 21-490B mass spectrometer as described in ref 7b. Replicate mass spectral data are reproducible to better than 0.4% of the base peak (equals 100.0%). All of the quantitative results reported are obtained from averages of three mass spectra, and are corrected for natural abundances of ¹³C and ¹⁵N. (b) P. Price, D. P. Martinsen, R. A. Upham, H. S. Swofford, Jr., and S. E. Buttrill, Jr., *Anal. Chem.*, **47**, 190 (1975).
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- (9) A blank reaction run for 20 hr without catalyst produces ~0.5% *d*₁ products.
- (10) Note that *d*₅-*d*₈ deuterated species are found (<1% of the total exchange products). Of these, the major product is *d*₆ followed by *d*₇, which indicates that the *d*₅-*d*₈ exchange products result from selective exchange at two ethyl groups.
- (11) Deuterium NMR spectra were run on an XL-100-15 FT spectrometer modified for multinuclear operation. CDCl₃ is used as internal standard. The relative integration of the CD₃- to the -CHD- is lower than predicted from the mass spectral analyses. This is probably attributable to different *T*₁ values for -CD₃ vs. -CDH-.
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Correlation Time Measurements of Amino Acid Side Chains from ¹H Selective Spin-Lattice Relaxation Rates

Sir:

Correlation times are routinely evaluated from ¹³C *T*₁ measurements,¹⁻⁴ but few determinations using ¹H *T*₁ techniques exist.⁵ Here we report correlation times derived from ¹H and ¹³C relaxation times in both concentrated and dilute solution of *N*-acetyl-*D*(*allo*)-isoleucine (1). This method is generally applicable to all molecules having a known geminal, or otherwise defined, interproton distance and has the advantage of applying to dilute solutions (in any solvent) or to molecules of greater molecular weight or complexity. It is not even necessary that the molecule have a determined crystal structure; the interproton distance could be derived from dihedral scalar coupling constants and the appropriate Karplus curve.

Many mechanisms, *m*, can determine proton relaxation pathways and, generally, if $R_1^i = 1/T_1^i$,

$$R_1 = \sum_{i,m} R_{1m}^i \quad (1)$$

In the extreme narrowing limit for the intramolecular dipole-dipole interactions of a proton, *i*, and all neighboring protons, *j*,