alkali atoms M and *unoriented* CH_3I molecules had been intensively studied by Herschbach and co-workers.[6] Comparison of their conclusions concerning the center-of-mass differential cross section and reaction-energy partitioning with those from trajectory calculations for the $K-CH_3I$ system on a number of different potential energy surfaces showed that an unequivocal distinction between the surfaces could not be made. For two of the surfaces (V_{MB} and V_S of ref 5b) we have now performed supplementary calculations with the same method as that employed previously[5] except that the initial conditions for each collision trajectory are altered: (a) rather than averaging over random initial orientations of CH_3I, only molecules with their axis parallel or antiparallel to the initial $K-CH_3I$ relative velocity vector are included, and (b) instead of averaging of a CH_3I rotational state population corresponding to a Boltzmann distribution at the beam temperature, only $J = 0$ molecules are selected. This choice of initial conditions provides a very simple approximate simulation of CH_3I molecules perfectly oriented by an external electric field. It does not prevent reorientation of the CH_3I molecules due to the interaction with the incoming K atom. However, this has been shown by trajectory analyses to be unimportant for the system under consideration, in agreement with the observation of Bernstein, *et al.*,[2] that their results are independent of the orienting voltage.

The most direct comparison of the scattering calculations is in terms of the total reaction cross section S_r. Table I gives the results obtained with surface V_{MB} and

Table I. Total Cross Sections (A^2) for Oriented and Unoriented Collisions[a]

	V_{MB}	V_S[b]
Unoriented[c]	25	13
$K \rightarrow CH_3I$	0	14
$K \rightarrow ICH_3$	35	11

[a] Results based on 500 trajectories with maximum impact parameter of 8 au. [b] The differences among the various V_S results are not significant. [c] The present experimental estimate of the total cross section for $K-CH_3I$ is 30 A^2; see ref 6.

V_S for unoriented CH_3I molecules and for the two initial orientations ($K \rightarrow CH_3I$ and $K \rightarrow ICH_3$). It is clear from the table that there is a sharp distinction between the surfaces in the orientation dependence of S_r: for V_{MB}, S_r is very sensitive to the initial orientation, while for V_S there is no correlation between the initial orientation and the magnitude of S_r. This is not to say that V_S scattering is independent of orientation; *e.g.*, the form of the differential cross section is altered by the orientation, with the sharp peaking in the backward direction for $K \rightarrow ICH_3$ reactive collisions shifted forward somewhat for $K \rightarrow CH_3I$ reactive collisions. Such a change is not surprising in view of the larger impact parameter collisions that contribute in the latter case. The final molecular rotational state distribution is correspondingly affected by the CH_3I orientation.

Comparison of the above results with the measurements[2,3] requires prior consideration of a number of

factors. First, a hopefully trivial point is that the orientation depends on the sign of the CH_3I dipole moment and all of the interpretation is based on the assumed choice $CH_3^+I^-$. Second, the state selection of the CH_3I molecules in the six-pole field achieves only a partial orientation, whose exact magnitude it is difficult to determine accurately. Thus, further work will be required to attempt to extrapolate the results to perfect orientation.[7] Third, measurements over only a small range of laboratory angles have been made, the angles being chosen to correspond to the maximum yield for the unoriented molecules. Thus, only an indication of the change in the total cross section is available, and there is left the possibility that part of the observed difference between the two initial orientations is due to a change in the center-of-mass angular distribution of the type found in the V_S collisions.[8]

In spite of the necessary cautions, the data appear to be sufficient to show that potential V_S is eliminated by the experimental asymmetry and to suggest that potential V_{MB} has the more appropriate form.[9,10] The essential difference between the two potential surfaces is that V_{MB} includes a $K-CH_3$ repulsion which makes the surface strongly dependent on the CH_3I orientation relative to the incoming K, while V_S lacks such a repulsion and is much closer to being spherically symmetric than V_{MB}. Thus, even these preliminary investigations clearly demonstrate that crossed beam experiments with oriented molecules provide an important new tool in the study of potential energy surfaces for reacting atoms and molecules.

(7) See also footnote 4 of ref 2.
(8) Bernstein, *et al.* (private communication), have also done measurements at somewhat smaller laboratory angles and find a lower asymmetry; the direction of the change is that indicated by the V_S results.
(9) To establish whether V_{MB} is too asymmetric will require more complete experimental alignment and more detailed calculations on partly oriented molecules. The calculations in ref 5b suggest a $\sin^2 (s/2)$ dependence as a crude approximation, where s is the angle between the I-K line and the $I-CH_3$ line.
(10) A recent analysis (D. R. Herschbach, private communication) of $K-CH_3I$ elastic scattering in terms of an effective two-body potential (E. F. Greene, A. L. Morsund, and J. Ross, *Advan. Chem. Phys.*, 10, 135 (1966)) indicates that the probability of reaction *vs.* impact parameter obtained from V_{MB} is more nearly correct than that from V_S (see ref 5b).
(11) Much of the work reported in this paper was done while both authors were in the Department of Chemistry, Columbia University, New York, N. Y.

M. Karplus[11]
*Department of Chemistry, Harvard University
Cambridge, Massachusetts*

M. Godfrey[11]
*Department of Chemistry, The University
Hull, England*

(6) For a review and references, see D. R. Herschbach, *Advan. Chem. Phys.*, 10, 319 (1966).

Comparison of Field Ionization and Chemical Ionization Mass Spectra of Decane Isomers

Sir:

Recently, a series of papers on a new mass spectrometric technique, called chemical ionization mass

Table I. Relative Ion Intensities in the Field Ionization and Chemical Ionization Mass Spectra of Eight Isomeric Decanes[a]

| | | 6 2-Me-5-Et-C7 | | 7 2,3,6-Me-C7 | | 8 2,4-Me-3-i-Pr-C5 | | 10 2,2,4-Me-C7 | | 11 2,2,6-Me-C7 | | 12 3,3,5-Me-C7 | | 13 2,2,3,3-Me-C6 | | 14 2,2,5,5-Me-C6 | |
m/e	Ion	FI	ChI	FI	ChI	FI	ChI	FI	ChI	FI	ChI	FI	ChI	FI	ChI	FI	ChI
142[b]	$C_{10}{}^+$	98.2	20.0	98.0	9.4	95.7	1.9	50.0	5.7	59.2	9.2	42.6	4.5	14.4	0.5	26.3	2.0
127	$C_9{}^+$	0.2	8.1	...	10.3	...	1.3	3.7	12.0	4.2	16.2	2.7	9.5	1.6	8.9	3.8	13.0
113	$C_8{}^+$	...	4.8	0.2	0.4	1.0	...	0.5	0.4	...	...	37.0	4.8	...	0.1	0.9	...
99	$C_7{}^+$	...	3.8	0.1	2.6	1.0	3.9	...	3.6	...	1.9	3.6	1.5	6.4	12.0	...	0.4
85	$C_6{}^+$	0.6R	14.0	0.3R	19.0	...	23.0	2.5	17.0	1.1	17.0	5.7	14.0	70.6	16.0	1.0	16.0
71	$C_5{}^+$	0.1	21.0	0.1	26.0	...	27.0	0.5	19.0	...	24.0	5.1	44.0	...	27.0	0.1	30.0
57	$C_4{}^+$	...	11.0	...	17.0	...	34.0	42.8	32.0	34.6	21.0	1.5	13.0	6.7	28.0	68.0	28.0
43	$C_3{}^+$	0.3	...	0.5	...	1.3	...	0.3	...	0.8	...	0.8	...	0.3	...	...	...
29	$C_2{}^+$	...	...	...	...	...	...	...	...	...	...	0.1	...	...	...	...	...
Σ minor ions		0.6	4.3	0.8	4.9	1.0	3.2	...	3.8	...	4.0	0.8	2.5	...	4.1	...	4.9
ΣI		100.0	87.0	100.0	89.6	100.0	94.3	100.1	93.5	99.9	89.1	99.9	93.8	100.0	96.6	100.1	94.3

[a] The compounds are numbered as found in ref 3. R = rearrangement peak with m/e 86 instead of 85. Isotopic peaks are not included into the table. Great bond fission with field ionization is indicated by arrows in the schematic molecular formulas. [b] m/e = 141 stands for 142 in the case of ChI.

Table II. Specification of Minor Ions as Noted in Table I and Metastable Ions in the FI Mass Spectra of Isomeric Decanes[a]

| | 2-Me-5-Et-C7 | | | 2,3,6-Me-C7 | | | 2,4-Me-3-i-Pr-C5 | | | 2,2,4-Me-C7 | | |
	Process	m/e	Rel int	Process	m/e	Rel int	Process	m/e	Rel int	Process	m/e	Rel int
Minor ions[b]		128	0.2		112	0.6		98	1.0			
		126	0.2		111	0.2						
		72	0.2									
Metastable ions	(P − 29)+	89.8	0.3	(P − 43)+	68.9	0.2	(P − 43)+	68.9	0.3	(P − 15)+	113.6	1.0
	(P − 30)+	88.3	1.5	(P − 44)+	67.7	0.9	(P − 44)+	67.7	3.2	(P − 16)+	111.8	1.2
				(P − 72)+	34.5	0.2				(P − 58)+	49.7	1.0

| | 2,2,6-Me-C7 | | | 3,3,5-Me-C7 | | | 2,2,3,3-Me-C6 | | | 2,2,5,5-Me-C6 | | |
	Process	m/e	Rel int	Process	m/e	Rel int	Process	m/e	Rel int	Process	m/e	Rel int
Minor ions[b]					98	0.2						
					84	0.6						
Metastable ions	(P − 15)+	113.6	0.8							(P − 15)+	113.6	0.3
	(P − 16)+	111.8	0.8							(P − 16)+	111.8	0.3
	(P − 58)+	49.7	1.1	(P − 58)+	49.7	0.4	(P − 58)+	49.7	0.7	(P − 85)+	23.6	?

[a] The metastable intensities are normalized to the total ion intensities. [b] Classification of minor ions from Table I.

spectrometry, has been submitted by Field and Munson.[1,2] This new technique seems to be very promising with respect to practical applications. Field, Munson, and Becker compared the chemical ionization (ChI) and electron-impact (EI) mass spectra of some paraffin hydrocarbons in the third paper of this series.[3] They stated that a comparison of chemical ionization and field ionization (FI) mass spectra could not be made at present because of lack of data on the latter. The FI mass spectra of eight isomeric decanes reported in the paper of Field, et al.,[3] have now been measured for the purpose of evaluating the fundamental difference of these two types of spectra. The results are given in Tables I and II.

Field, et al., were able to rationalize the observed ChI mass spectra by a set of simple postulates of the reactions occurring. Moreover, they succeeded in estimating the relative abundances of the MW − 1 ions

in terms of the number of "available" hydrogen atoms. A quantitative calculation of the relative ion abundances is not possible with field ionization at present. However, some general rules can be stated.

(1) The stability of the molecular ions formed by FI is much higher than that of the MW − 1 ions formed by ChI.

(2) The places of greatest bond fission in FI are quite different from those in ChI.

(3) A weak and unspecific fragment spectrum arises from FI in the case of molecules containing several tertiary carbon atoms.

(4) Intense fragment ions are formed with FI of compounds containing quaternary carbon atoms. The charge is stabilized mainly at the larger of two fragments if two quaternary carbon atoms are contained in a molecule.

Concerning rule 1, carbonium ions are formed with ChI (even number of electrons) and molecular ions are formed with FI (uneven number of electrons). An energetically favorable bond fission is possible if ChI occurs at a C–H bond in a position β to a branch. This is not possible with FI.

(1) M. S. B. Munson and F. H. Field, J. Am. Chem. Soc., 88, 2621 (1966).
(2) M. S. B. Munson and F. H. Field, ibid., in press.
(3) F. H. Field, M. S. B. Munson, and D. A. Becker, Advances in Chemistry Series, American Chemical Society, Washington, D. C., in press.

Concerning rule 3, the positive charge of the molecular ion is not concentrated at a point near one end of the molecule, as in normal paraffins,[4] which are ordered parallel to the electrical field lines,[5] but is distributed over the points of the branches. This reduces the fragmentation probability per branch as compared with a singly branched or a normal paraffin.

Concerning rule 4, the same argument holds as mentioned under (3), but the bonds of quaternary carbon atoms are so weak that field dissociation is possible to a large extent.

Acknowledgment. The author thanks Dr. F. H. Field for providing the isomeric decanes and Mr. K. G. Hippe for assistance with the measurements.

(4) H. D. Beckey, Z. Naturforsch., 19a, 71 (1964).
(5) H. D. Beckey, ibid., 17a, 1103 (1962).

H. D. Beckey

Institut fuer Physikalische Chemie der Universität Bonn
Bonn, West Germany

Equilibration of 2-Methylnorbornanols. A Fast Acid-Catalyzed Conversion of 2-Methyl-exo-norbornanol into 2-Methyl-endo-norbornanol

Sir:

It is our pleasure to report that the acid-catalyzed equilibration of 2-methyl-, 1,2-dimethyl-, and 2-phenyl-exo-norbornanols reveals approximately equal stabilities for the exo and endo tertiary isomers. These results render untenable the argument that the similarity in the exo/endo rate ratios observed in the solvolysis of norbornyl, 2-methylnorbornyl, and 2-phenylnorbornyl derivatives[1] results from a fortuitous cancelation of increasing steric assistance in this series with decreasing σ participation by the 1,6-electron pair.[2]

We further wish to report that under the influence of aqueous acids 2-methyl-exo-norbornanol is converted into the endo isomer, 2-methyl-endo-norbornanol, at a rate twice that at which it forms the exo derivative, 1-methyl-exo-norbornanol. This result does not appear to be compatible with the formulation of the carbonium ion intermediate as a bridged, nonclassical species (I).
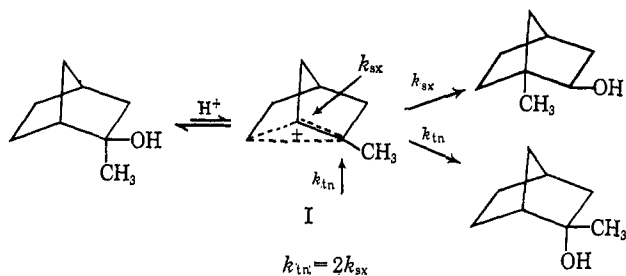
The equilibration was initially carried out by stirring each of the alcohols dissolved in cyclohexane with an equal volume of aqueous sulfuric acid (2, 4, and 6 *M*) at room temperature. Aliquots were removed at

(1) H. C. Brown, F. J. Chloupek, and M. -H. Rei, J. Am. Chem. Soc., 86, 1248 (1964).
(2) P. von R. Schleyer, Symposium on Linear Free Energy Correlations, U. S. Army Research Office, Durham, N. C., Oct 19–21, 1964. See discussion in the review by M. J. S. Dewar and A. P. Marchand, Ann. Rev. Phys. Chem., 16, 321 (1965).
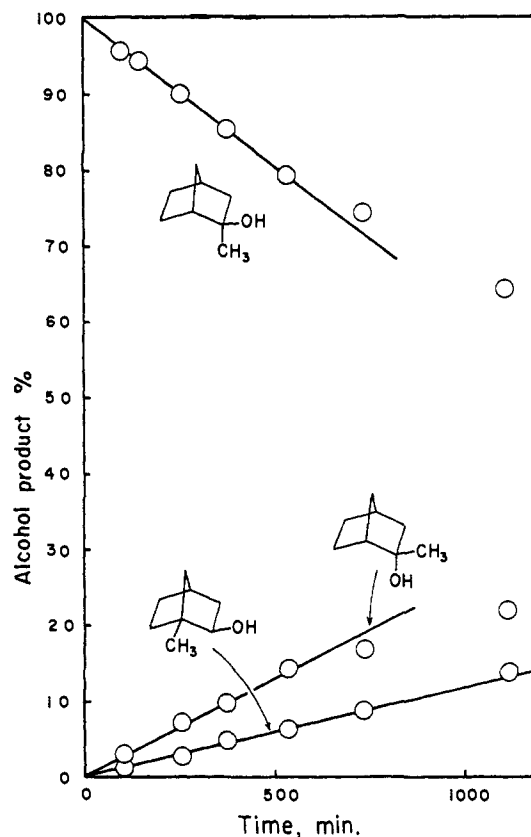
Figure 1. Acid-catalyzed solvolysis at 25° of 2-methyl-exo-norbornanol in 60% aqueous dioxane, 1.75 *M* in perchloric acid.

appropriate intervals of time and analyzed by capillary gas chromatography. We were surprised by the observation that 2-methyl-endo-norbornanol was being formed at twice the rate of 1-methyl-exo-norbornanol in the initial phases of the equilibration of 2-methyl-exo-norbornanol.[3] In order to eliminate the possibility that this was an artifact of the heterogeneous conditions, we repeated a number of the experiments utilizing the homogeneous conditions adopted by Bunton for his oxygen-18 exchanges, namely 1.75 *M* perchloric acid in 60% aqueous dioxane.[4] As shown by the data in Figure 1, the results fully confirm the conclusion that the cation from 2-methyl-exo-norbornanol undergoes substitution by the solvent at the endo tertiary position at a rate twice that at which it undergoes substitution at the exo secondary position.

At equilibrium[5] we observed that the ratio of 1-methyl-exo-, 2-methyl-exo-, and 2-methyl-endo-norbornanol is 3.6:1.3:1.00. In the case of 1,2-dimethyl-exo-norbornanol, the exo/endo product ratio is 2.6. In the 2-phenyl system, the exo/endo product ratio for the tertiary alcohols[3] is 2.1. In all cases the equilibrium value was approached starting with two or more isomeric alcohols.

The exo/endo equilibrium ratio of 1.3 obtained for 2-methyl-exo- and -endo-norbornanols is actually in good

(3) Perhaps even more remarkable, either isomer of 2-phenyl-2-norbornanol could be converted into the equilibrium mixture of tertiary isomers before any significant amount of the secondary isomer appeared.
(4) C. A. Bunton, K. Khaleeluddin, and D. Whittaker, Tetrahedron Letters, 1825 (1963).
(5) The rate of formation of 1-methyl-endo-norbornanol was very slow. Consequently, we were content to establish essential equilibrium among the more reactive isomers.

Communications to the Editor