bonded interaction of carboxyl groups and benzene hydrogens in the transition state is likely to contribute significantly to the destabilization of the transition state. Work is in progress to settle this question by studies of the resolvability (and optical stability) of Id and of other dissymmetric cyclooctatetraenes.

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NEGATIVE TEMPERATURE COEFFICIENTS FOR ION-MOLECULE REACTIONS

Sir:

Stevenson and Schissler[1,2] observed a "small but real" negative temperature coefficient for the cross-section of reactions between hydrocarbon ions and molecules. The phenomenological cross-section is inversely proportional with the repeller field strength in these cases. Gioumousis and Stevenson[2] calculated also the relation between the phenomenological cross-section Q and the microscopic cross-section σ for reactions between molecular ions and molecules when the rate of reaction is determined only by the interaction between a charge and an induced dipole, *i.e.*, when σ is inversely proportional to the relative velocity g at a large distance between ion and molecules. In this case Q is found to be inversely proportional to the square root of the repeller field strength, and independent of temperature.

It has been pointed out by Hamill and Boelrijk[3,4,5,6] that a variation of Q inversely proportional to the repeller field strength occurs when the average value of σ for velocities of the ion at the exit slit is practically zero. It also has been found experimentally that σ for ion-molecule reactions in cyclopropane[4] and in neopentane[5,6] can be described adequately by functions of the form $\sigma(\epsilon) = \sigma_1 \epsilon^{-1/2} - \sigma_H$, for $\epsilon \leqslant \epsilon_c$ and $\sigma(\epsilon) = 0$ for $\epsilon \geqslant \epsilon_c$, where ϵ is the kinetic energy of the ion, and ϵ_c, σ_1 and σ_H are constants. This suggests that $\sigma(g) = (g_c/g - 1)\sigma_H$ for $g \leqslant g_c$ and $\sigma(g) = 0$ for $g \geqslant g_c$ is a suitable model. The constant σ_1 is presumably equal to the cross-section for a collision in the ion induced dipole model at 1 eV. relative kinetic energy multiplied by an efficiency factor for the reaction under consideration. The physical meaning of σ_H is not clear, though it may be related to nearly head-on collisions.

An examination of Gioumousis and Stevenson's derivation shows that no temperature effect occurs, if the product $g\sigma(g)$ is a constant. An example will be given that a negative temperature coefficient can be found for the phenomenological cross-section without introducing a temperature effect in the microscopic cross-section when $g\sigma(g)$ is a decreasing function of g.

(1) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **24**, 926 (1956).

(2) G. Gioumousis and D. P. Stevenson, *ibid.*, **29**, 294 (1958).

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We considered the trajectories of two ions starting with equal velocities but in opposite direction from a point in the plane of the mass spectrometer electron beam. These trajectories are parts of a parabola. The trajectories can be replaced by the trajectories of two hypothetical ions starting in the top of the parabola, with the same velocity components as the former ions in directions perpendicular to the repeller field and no velocity in the direction of the field. This replacement is allowed if the number of primary ions does not change appreciably due to reactions. The influence of the initial velocity distribution in the direction of the field will be found back in the upper limit of the integral over the trajectories of the ions within the ionization chamber. This influence will be neglected as the contribution to the reaction is very small when the velocity of the ion in the laboratory reference system is much larger than g_c.

The sixfold integral which has to be evaluated becomes now

$$i_s/i_p = N \int \sigma(g) f_{x1} f_{y1} f_{x2} f_{y2} f_{z2} dv_{x1} dv_{y1} dv_{x2} dv_{y2} dv_{z2} ds$$

where f_{x1} is the Maxwell–Boltzmann distribution function of the velocity v_{x1} of the ion in the x direction, *etc.* The indices 1 and 2 are used to indicate, respectively, the ion and the molecule; the homogeneous electric field is taken in the z direction; i_p and i_s are, respectively, the primary and secondary ion current; ds is an element of the relative path of an ion–molecule pair[7] and N the density of the molecules.

Taking $\sigma(g) = C_1/g$, it is easily derived that

$$Q = i_s/i_p \times 1/Nd_0 = C_1(2m_1/eEd_0)^{1/2}$$

which is equivalent to Gioumousis' expression (17).[2] E is the electric field strength and d_0 is the distance between electron beam and exit slit.

Evaluation of the integral for $\sigma(g) = (g_c/g - 1)\sigma_H$ yields

$$Q = \frac{2kT}{eE_0 d_0} \frac{m_1}{\mu} \sigma_H \left\{ \frac{1}{2} w^2 - \int_0^w e^{-y^2} dy \int_0^y e^{x^2} dx \right\}$$

where the dimensionless quantity w is given by $w = (\mu/2kT)^{1/2}g_c$. Tables of the value of the integral as function of w have been published.[8]

The temperature effect can be found by calculating Q at different temperatures. The results of such calculations for $eEd_0 = 2$ eV. and for three reactions are presented in the table.

Reaction	σ_1 (eV.$^{1/2}$Å.^{2})	σ_H (Å.^{2})	T (°K.)	Q (Å.^{2})
$C_2H_4^+ + C_2H_4{}^a$	49.2	40.0	400	26.8
			500	26.3
			600	25.6
$CH_3OH^+ + CH_3OH^a$	42.8	49.4	400	14.8
			500	14.3
			600	13.7
$CS_2^+ + neo\text{-}C_5H_{12}{}^b$	5.3	3.1	400	0.422
			500	0.420
			600	0.413

^{a} Estimated, see p. 35 of ref. 6; no efficiency factor f taken into account. The relative change of Q with temperature does not depend on f, unless f changes with temperature. ^{b} Measured, see p. 106 of ref. 6.

(7) The perturbation of the path by the ion-induced dipole interaction is accounted for by the use of the cross-section.

(8) J. Barkley Rosser, "Theory and Application of . . . (some integrals)," Mapleton House Publishers, Brooklyn N. Y., 1948.

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XENON TETRAFLUORIDE[1]

Sir:

The first true compound of xenon, $Xe^+PtF_6^-$, recently was reported by Bartlett.[2] This suggested to us the possibility that under some conditions of temperature and pressure xenon might be oxidized by elemental fluorine. We have now found that xenon and fluorine react readily to form a solid compound XeF_4 that is stable at room temperature.

One part xenon and approximately five parts of fluorine by pressure were mixed in a 130 cc. nickel weighing can. The mixture was heated at 400° for one hour and then cooled rapidly to room temperature with a water bath. The can was weighed before and after admitting the xenon and again after the reaction when the excess fluorine had been pumped off with the can in a −78° bath. The fluorine was pumped through a U-tube in a −195° bath in order to collect any unreacted xenon. No unreacted xenon was found when the reactions were carried out with excess fluorine. A separate experiment with pure xenon had established that it can be caught quantitatively in a −195° bath.

Table I shows the results of formula determinations based on the combining weights of xenon and fluorine.

TABLE I

CHEMICAL FORMULA OF XENON FLUORIDE

Preparation	Xe taken, millimoles	F_2 consumed, millimoles	Atom ratio F/Xe
1	2.248	4.558	4.05
2	1.806	3.539	3.92
3	1.944	3.808	3.91
4	2.745	5.453	3.97

In another method to verify the formula, a weighed sample of the compound was heated in a weighing can with excess hydrogen at 400° to form hydrogen fluoride and xenon. The excess hydrogen was pumped off with the can in a −195° bath. The material was then distilled under high vacuum through two nickel U-tubes in series. The first was in a −159° bath so as to trap the hydrogen fluoride and pass the xenon. The second U-tube was in a −195° bath to trap the xenon. The xenon was transferred to a weighing can and weighed and its identity and purity checked by mass spectrometric analysis. The hydrogen fluoride was weighed, hydrolyzed in a known excess of NaOH and determined both by back titration with HCl and a fluoride analysis. The reduction was found to proceed according to reaction (1)
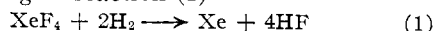
$$XeF_4 + 2H_2 \longrightarrow Xe + 4HF \qquad (1)$$

Total XeF_4 taken: 0.4006 g.; Xe: found 0.2507 g., calculated 0.2537 g.; F: found 0.1435 g., calculated 0.1469 g.; HF: found 7.53 milliequivalents, calculated 7.73 milliequivalents.

Xenon tetrafluoride is a colorless solid. It has a negligible vapor pressure at −78° and roughly 3 mm. at room temperature. It can be sublimed easily at room temperature. Samples of XeF_4 sealed under vacuum in a glass tube grow to large, colorless crystals within a few hours.

The compound is stable at room temperature and has been stored unchanged in nickel or glass vessels for over a week. XeF_4 in a thin-walled Pyrex capillary was observed not to melt up to 100°.

Xenon tetrafluoride appears to be insoluble in and does not react with $n\text{-}C_7F_{16}$.

A preliminary scan of the infrared spectrum of the vapor has been made from 4000 to 400 cm.$^{-1}$, and only one strong band was found. This is at 590 cm.$^{-1}$, in the region where fluorine–metal stretching frequencies usually are found. That there is only one stretching frequency indicates high symmetry of the gaseous molecule, consistent with either a tetrahedral or square planar structure.

Several weighed samples of XeF_4 were hydrolyzed with dilute NaOH and the total amount of evolved gases was determined by PVT measurements. Upon hydrolysis with either dilute NaOH or H_2O, a yellow product was formed which slowly dissolved to give a clear, pale yellow solution. One might expect the hydrolysis to proceed according to the reaction

$$XeF_4 + 2H_2O \longrightarrow Xe + O_2 + 4HF \qquad (2)$$
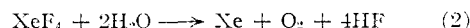
Analysis for total fluoride is in agreement with this equation. However, the amount of gas liberated and the ratio of xenon to oxygen are not in agreement with equation (2). This indicates that the chemistry of hydrolysis is more complex. The nature of the hydrolysis reaction is being investigated further.

Preliminary studies of the reaction of fluorine or XeF_4 with excess Xe at 400° indicate the existence of a lower fluoride of xenon.

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PRODUCTION AND REACTIONS OF METHYLENE IN THE TRIPLET STATE

Sir:

Unlike singlet methylene,[1-4] the ground state triplet[5] is difficult to generate in the vapor phase.[5,6,7] However, inasmuch as the spin angular momentum is conserved in mercury photosensitized reactions, as believed, it would be expected that in the triplet mercury (Hg 6^3P_1) photosensitized decomposition of ketene and diazomethane triplet methylene

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