an efficient proton scavenger.[11] Our data indicate that a trace of NH_3 (1.5 mole %) completely stops the disappearance of CD_4. This effect is similar to that of Xe in the radiation-induced H_2–D_2 exchange.[2] Preliminary experiments indicate that Xe is not effective as a proton scavenger in the CH_4–D_2 system. Findings to date indicate that proton-transfer efficiencies may be ranked in the order $NH_3 > CH_4 > Xe > D_2$, and that this order may be the same as that for the proton affinities of these molecules. Judicious use of NH_3 to block ionic reactions in the D_2–TD–CH_4 system may permit accurate evaluation of the temperature coefficient for the atomic exchange reaction. Work directed toward establishment of a more inclusive scale of relative proton-transfer efficiencies and toward elucidation of the atomic and free-radical exchange mechanism for CH_4 and D_2 is in progress.[12]

(11) M. A. Bonin, W. R. Busler, and F. Williams, *J. Am. Chem. Soc.*, **84**, 4355 (1962).
(12) This work is partially supported by U.S.A.E.C. Contract AT-(11-1)-116.
(13) Captain, U.S.A.F., A.F.I.T. Program 1961-1965.

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The Heat of Formation of Xenon Tetroxide[1]

Sir:

The preparation and some properties of XeO_4 have been recently described.[2,3] In the present work, the heat of explosive decomposition of the gas to its constituent elements at 25° has been measured.
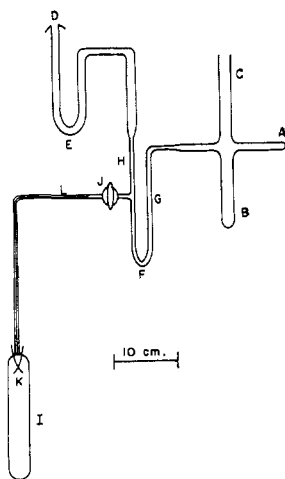

Figure 1. Preparation and explosion system.

The preparation was performed essentially according to the procedure previously given,[3] using the glass apparatus shown in Figure 1. Anhydrous sodium perxenate, 40 to 80 mg. (Peninsular ChemResearch, Gainesville, Fla.), was placed at A and *ca.* 5 ml. of

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.
(2) J. L. Huston, M. H. Studier, and E. N. Sloth, *Science*, **143**, 1161 (1964).
(3) H. Selig, H. H. Claassen, C. L. Chernick, J. G. Malm, and J. L. Huston, *Science*, **143**, 1323 (1964).

previously boiled sulfuric acid at B; the system was then sealed off at C and evacuated overnight through D with a −196° bath at E. The apparatus was then inclined slightly counterclockwise, a 0° bath placed at B and a −126° bath at F, and the salt slowly added to the acid by occasional tapping at A over a period of *ca.* 0.5 hr. The system was then sealed off at G, a −196° bath placed at F, and the system again sealed at H. The 90-ml. explosion cell I was then placed in the aneroid copper-block calorimeter previously described.[4] After recording of the foredrift, the −196° bath was removed from F and a warm-air blower, *ca.* 50 cm. distant, was played on trap F. The solid in the trap was seen to disappear in about 40 sec., and, about 15 sec. later, stopcock J was closed and the gas immediately exploded by passing a spark from a 0.1-μf. capacitor at 600 v. across the loosely contacting tungsten electrodes K. A blue flash was seen to pass up the 1-mm. i.d. capillary from I to J. About 1.5 min. later, the capillary was sealed off at L.

After the calorimetric measurement, the cell was attached to a gas-measurement line and the oxygen was transferred through three traps at −196° to a buret by means of a Toepler pump. The third trap was then warmed to −78° and the first two to room temperature to determine the xenon. The third trap was then warmed to room temperature; gas, probably mostly water, amounting to from 0.2 to 2% of the xenon was found. The oxygen and xenon were analyzed mass spectrometrically; a little xenon was found in the oxygen and a little carbon dioxide in the xenon. Appropriate corrections were applied to the measured amounts.

Of 24 preparations performed, 15 detonated in the trap F during warming, 2 failed to explode upon sparking, perhaps owing to very rapid previous nonexplosive decomposition to the elements, and the gas from 2 runs was lost after a successful explosion. Results for the successful runs are given in Table I. The yield of

Table I

| | | —μmoles— | | |
Run	q, cal.	O_2	Xe	$-\Delta H$, kcal. mole^{-1}
1	7.17	92.4	45.7	154.2
2	4.58	58.9	29.3	154.2
3	7.54	98.2	49.0	152.0
4	6.33	80.9	40.8	154.0
5	6.56	84.7	42.4	152.9

XeO_4 in the preparations ranged from 20 to 35%. The oxygen:xenon ratios found range from 1.984 to 2.022, equal to the theoretical value of 2 within experimental limits. The average of the xenon and one-half of the oxygen is used to calculate ΔH. nRT is subtracted from q to correct for the pV work done by the entering gas, and $2RT$ is subtracted from q_{cor}/n to convert from $-\Delta E$ to $-\Delta H$. The average is −153.5 for $\Delta H°$ of the reaction
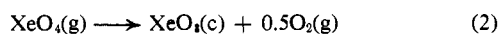
$$XeO_4(g) \longrightarrow Xe(g) + 2O_2(g) \qquad (1)$$
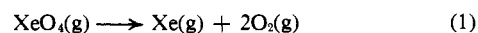
or +153.5 for $\Delta H_f°(XeO_4,g)$.

Huston, *et al.*,[2] observed a nonexplosive decomposition of highly variable rate, yielding at least partly

(4) S. R. Gunn, *Rev. Sci. Instr.*, **35**, 183 (1964).

XeO₃. The standard heat of formation of XeO$_3$(c) has been determined[5] to be 96 ± 2 kcal. mole^{-1}; hence the heat of the reaction

$$XeO_4(g) \longrightarrow XeO_4(c) + 0.5O_2(g) \qquad (2)$$

would be −58 kcal. mole^{-1}. The agreement of the observed Xe:O₂ ratio with the theoretical indicates either that reaction 2 did not occur to any significant extent or that the XeO₃ produced was itself subsequently decomposed to the elements. Any production of XeO₃ in the cell I and subsequent detonation by the XeO₄ explosion would introduce no error since the sum heat would still be that of reaction 1. Any XeO₃ deposited in the capillary and subsequently exploded would introduce an error since its heat would not be delivered to the calorimeter but the xenon and oxygen produced would be measured, and in the expected ratio. Three factors suggest that this possible error cannot have been serious: the short residence time of XeO₄ in the capillary while flowing to the cell; the consistency of the five runs; and the fact that runs 1, 2, and 3 used an ordinary glass high-vacuum stopcock lubricated with Kel-F grease while runs 4 and 5 used a Springall greaseless diaphragm-type valve with Viton A diaphragm; absorption in the grease or reaction with the diaphragm are thus unlikely to have been significant.

Using 119 kcal. mole^{-1} for the dissociation energy of oxygen,[6] the thermochemical bond energy in XeO₄ is 21.1 kcal. For XeO₃, the value is $27.5 - \Delta H_{sub}/3$; the vapor pressure of XeO₃ is very low and ΔH_{sub} is unknown. However, Studier[7] observed the molecular mass spectrum of XeO₃ with a source at room temperature, with the intensity increasing rapidly as the temperature was raised slightly; an estimate of 30 ± 10 kcal. mole^{-1} for ΔH_{sub}(XeO₃) might be made. The Xe–F thermochemical bond energies are approximately 28 kcal.[8] for XeF₂, 30[9] or 32[10] for XeF₄, and 32[10] for XeF₆. Thus the energy of the Xe=O bond is substantially less than that of Xe–F, but like Xe–F varies little with the oxidation number of the xenon.

From these bond energies, one may estimate −6 kcal. mole^{-1} for the standard heat of formation of gaseous XeOF₄, and +56 kcal. mole^{-1} for XeO₂F₂.

(5) S. R. Gunn, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p. 149.
(6) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworth Scientific Publications, London, 1958.
(7) M. H. Studier, unpublished observations, Argonne National Laboratory, 1964.
(8) B. Weinstock, E. E. Weaver, and C. P. Knop, ref. 5, p. 50.
(9) S. R. Gunn and S. M. Williamson, ref. 5, p. 133.
(10) L. Stein and P. Plurien, ref. 5, p. 144.

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Equilibria between Metallic Sodium and Aromatic Hydrocarbons[1]

Sir:

In the course of investigations of the formation[2] and degradation kinetics of vinyl aromatic polyradical

(1) This paper represents one phase of research performed by the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration, Contract NAS7-100.
(2) A. Rembaum and J. Moacanin, *J. Polymer Sci.*, **B1**, 41 (1963).

anions[3] a pronounced temperature effect was observed on the visible spectra of the poly(vinylbiphenyl)– and poly(N-vinylcarbazole)–sodium complexes, as well as on the complexes of the corresponding ethyl-substituted aromatic hydrocarbons dissolved in tetrahydrofuran (THF). The temperature effect could not be attributed to variation of volume changes due to thermal contraction or expansion, since the apparent extinction coefficient and also the free spin concentration as determined by the electron spin resonance technique[3] (e.s.r.) varied by as much as a factor of six to seven. This loss of paramagnetism with increase of temperature was previously assumed[4] to be a result of a disproportionation reaction leading to the formation of dinegative ions. Our data indicate that this interpretation does not apply to our systems. Although the intensity of the e.s.r. signal increased markedly with temperature decrease, the wave lengths of the absorption peaks in the visible part of the spectrum remained unchanged over a wide temperature range, suggesting that no new complexes were being formed. Since metallic sodium does not dissolve in THF,[3,5] these facts are therefore consistent with the postulated equilibrium[6] between sodium and aromatic hydrocarbons; the equilibrium was confirmed by the isolation of pure sodium after warming to room temperature a THF solution of [N-ethylcarbazole]$^-$Na$^+$ or [4-ethylbiphenyl]$^-$Na$^+$ prepared at −70°. The phenomenon is completely reversible, with the sodium particles dissolving and the blue color darkening upon cooling.

Although equilibria between alkali metals and aromatic hydrocarbons have been considered previously[7] and a reversible color change was noted,[8] the influence of temperature on the extinction coefficients of charge-transfer bands exhibited by alkyl-substituted hydrocarbon radical anions has, to our knowledge, never been investigated, and the temperature-induced reversible precipitation of an alkali metal associated with an aromatic radical anion has not been observed.

In this communication we summarize the preliminary results of a quantitative study of the equilibria between sodium and some substituted aromatic hydrocarbons by a spectrophotometric technique.

The absorption spectrum of [N-ethylcarbazole]$^-$Na$^+$ recorded at three different temperatures in the wave length range of 300 to 500 mμ is shown in Figure 1. The charge-transfer band at 390 mμ shows a remarkable change with temperature, while the bands at 350 mμ and below change only slightly.[9] The latter originate from electronic transitions which are not affected by the extra electron, in agreement with the interpretation given previously.[10] The variation of the absorbance

(3) A. Rembaum and co-workers, to be published.
(4) E. deBoer, *Advan. Organometal. Chem.*, **2**, 115 (1964).
(5) F. Cafasso and B. R. Sundheim, *J. Chem. Phys.*, **31**, 809 (1959); F. S. Dainton, D. M. Wiles, and A. N. Wright, *J. Chem. Soc.*, 4283 (1960).
(6) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).
(7) G. J. Hoijtink, E. deBoer, P. H. Van der Meij, and W. B. Weijland, *Rec. trav. chim.*, **74**, 277 (1955); *ibid.*, **75**, 487 (1956).
(8) S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 6462 (1958).
(9) The spectrum between 300 and 350 mμ (Figure 1) is identical with the spectrum of unreacted N-ethylcarbazole in this wave length range.
(10) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956).