Figure 2. Chemical shift of DMSO protons vs. DMSO/MX mole ratio: A, NH₄SCN; B, NaI; C, blank.

nificantly from those for Li^+ or NH_4^+ in that its slope is much less, indicating a strong interaction even at mole ratios as high as 9:1. There seems to be some indication of a break at 1:1 mole ratio which would agree with the results of Schaschel and Day,[5] but in our system the break is much less pronounced and may not be significant. It seems reasonable to assume that while sodium ion is solvated by DMSO, in our system the stoichiometry is much less well defined than in the case of lithium. This observation is in accord with the usual behavior of Li^+ and Na^+ ions in solutions.

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Tellurium in the Formal Electropositive Oxidation State One-Half in Acidic Chloride Media

Sir:

We are investigating the redox chemistry of tellurium in molten acidic chloride salt media and report here strong evidence that a polynuclear tellurium ion with the formal electropositive oxidation state one-half occurs in solution. We also have evidence for another polynuclear tellurium ion with an electropositive oxidation state but have not as yet established its formal oxidation number. Our experimental approach has been like that used to study the lower electropositive oxidation states of bismuth in molten salt solutions.[1]

Small amounts of elemental tellurium react with dilute solutions of $TeCl_4$ in the molten $AlCl_3$–$NaCl$ eutectic to yield purple solutions having the spectrum shown in Figure 1. (In Figure 1 the absorbance has been cor-

(1) N. J. Bjerrum, C. R. Boston, G. P. Smith, and H. L. Davis, *Inorg. Nucl. Chem. Letters*, **1**, 141 (1965); N. J. Bjerrum and G. P. Smith, *ibid.*, **3**, 165 (1967); N. J. Bjerrum, C. R. Boston, and G. P. Smith, *Inorg. Chem.*, **6**, 1162 (1967); H. L. Davis, N. J. Bjerrum, and G. P. Smith, *ibid.*, **6**, 1172 (1967); N. J. Bjerrum, H. L. Davis, and G. P. Smith, *ibid.*, **6**, 1603 (1967); N. J. Bjerrum and G. P. Smith, *ibid.*, **6**, 1968 (1967).
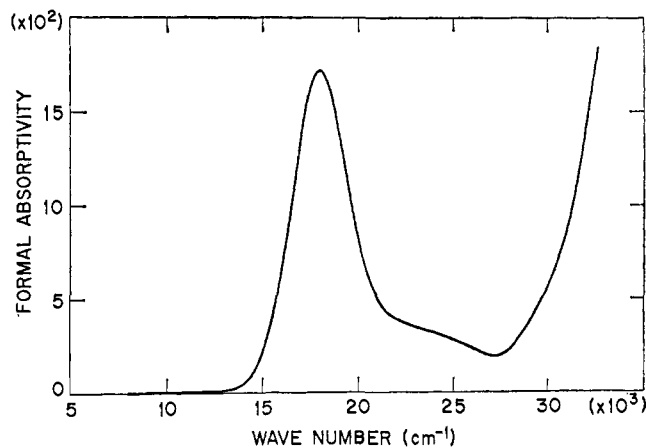

Figure 1. Adsorption spectrum of Te_{2n}^{n+} in the molten $AlCl_3$–NaCl eutectic.

rected for overlap by the spectrum of $TeCl_4$ in the ultraviolet.) As long as the mole ratio $Te/TeCl_4$ is less than 7, the absorbance of these solutions is proportional to the amount of elemental tellurium added and only slightly affected by changing the temperature. When the $Te/TeCl_4$ mole ratio is increased to 7 and beyond, the absorbance at the principal band peak passes through a maximum and starts decreasing. The mole ratio of 7 at which this change occurs is independent of temperature and the initial $TeCl_4$ concentration over substantial ranges, and the estimated error in the value of this mole ratio is less than 1%.

We conclude that up to the mole ratio 7, only one entity is formed, and that it has the stoichiometry

$$7Te + Te^{4+} = \frac{4}{n}Te_{2n}^{n+}$$
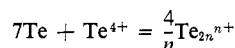
At the mole ratio 7, virtually all of the tellurium is present as Te_{2n}^{n+}, and at higher mole ratios another tellurium entity is formed with a formal oxidation number between $1/2$ and 0.

We have not established the exact value of n in Te_{2n}^{n+}, but present data indicate it is not very different from 2, so that our best guess at the moment is that Te_4^{2+} is formed. This estimate of n is based on studies of two sets of inhomogeneous equilibria analogous to those previously described for bismuth.[1] An even value of n seems plausible because of the expectation that an even number of bonding electrons is involved. Our data give no information on whether or not this entity is bound in any way to chlorides or chloroaluminates.

As an interesting side experiment, we fused together Te, $TeCl_4$, and $AlCl_3$ in the mole ratio 7:1:4 and obtained a dark purple (almost black) product which we zone-melted without evidence of segregation; samples from different parts of the bar melted sharply at 228 ± 0.5° and gave the same X-ray powder patterns. Possibly this is a compound (stoichiometric composition Te_2AlCl_4) which contains Te_{2n}^{n+}.

It seems likely that Te_{2n}^{n+} is related to Se_4^{2+}, reported by Barr, Gillespie, Kapoor, and Malhotra[2] earlier this year.

Research continues on determining the value of n for Te_{2n}^{n+} in solution and the identity of the products

(2) J. Barr, R. J. Gillespie, R. Kapoor, and K. C. Malhotra, *Can. J. Chem.*, **46**, 149 (1968).

formed when Te and TeCl$_4$ react with a mole ratio greater than 7.

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On the Origin of Bond-Energy Effects on Hot Hydrogen Abstraction[1]

Sir:

In a series of communications and articles,[2-4] Rowland and collaborators have established that the yield of the hydrogen-abstraction reactions of hot tritium atoms with hydrocarbons is remarkably sensitive to the

$$RH + T \longrightarrow HT + R$$
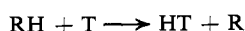
strength of the R–H bond being broken. Several explanations of this phenomenon, unusual for hot-atom processes, have been offered. (A) An early suggestion was that the RH–T intermediate was sufficiently long-lived to undergo reasonably normal unimolecular decomposition. This would favor reaction involving rupture of the weak bond. Subsequently, however, it has become accepted that formation of such long-lived complexes was highly unlikely, at least with alkanes. (B) It was then postulated that one possible contribution to the bond-energy effect might be the existence of lower thresholds for abstraction in systems having weaker R–H bonds.[2,4] Although qualitatively reasonable, kinetic theory calculations[5] indicate that this explanation is quantitatively inadequate to account for the observed magnitudes. (C) Instead, it was proposed[5] that the effect was due to abstraction taking place in high-energy stripping or glancing collisions. In such interactions, the high energy of the hot atom is, for the most part, not available to break the R–H bond and drive the reaction. Thus differences of the order of a few kilocalories in the bond strengths might greatly affect the efficiency of reaction.

Hypothesis B predicts that the lower the energy of the C–H bond the lower will be the average energy of hot-atom abstraction. Hypothesis C predicts that a weaker bond will promote abstraction by the high-energy stripping mechanism and will therefore raise the average energy of abstraction. In this communication, we report measurements on the trends of mean energy of hot abstraction as a function of bond energy. Such data indicate that hypothesis C is probably dominant for recoil tritium.

Hot hydrogen in the form of recoil tritium produced by the He^3(n,p)T process was generated in various mixtures of protonated and deuterated alkanes. Irradiation and analytical procedures were as described else-

(1) This work was supported by the U. S. Atomic Energy Commission.

(2) J. Root and F. S. Rowland, *J. Am. Chem. Soc.*, **84**, 3027 (1962).

(3) W. Breckenridge, J. Root, and F. S. Rowland, *J. Chem. Phys.*, **39**, 2374 (1963).

(4) J. Root, W. Breckenridge, and F. S. Rowland, *ibid.*, **43**, 3694 (1965).

(5) R. Wolfgang, *Progr. Reaction Kinetics*, **3**, 97 (1965); see particularly pp 134, 139–141; *Ann. Rev. Phys. Chem.*, **16**, 31 (1965).

where.[6,7] The tritium atoms are produced at very high velocities and lose energy in successive collisions until they react or are thermalized and removed by Br$_2$ scavenger (present in all samples). In pure hydrocarbons, most atoms react at relatively high energies. Upon addition of an inert gas moderator, neon in this work, the probability of collision with reactant is diminished. More atoms thereby survive to have the chance to react at lower energies. Hence while all yields tend to decrease, those of low-energy processes will normally be diminished less.[8] Consequently, the ratio of high-energy hot reaction to low-energy hot reaction will drop with moderation.

Figure 1 shows the effect of moderation on the ratio HT/DT produced by hot reaction in an equimolar mixture of CD$_4$ and C$_2$H$_6$. It appears that abstraction from C$_2$H$_6$ occurs at a higher mean energy than from CD$_4$.[8] Since the C–H bond strength of C$_2$H$_6$ is 98.0 kcal while that of CD$_4$ is 104.7 kcal, it is the prediction of hypothesis C that is followed.

Table I summarizes results on moderation in six mixed systems. In every case, abstraction at the weaker C–H bond seems to occur at higher average

Table I

Reaction mixture	HT/DT yield ratio		Mean rel abstr energy	Bond energy,[b] kcal
	No moderation	100% moderation[a]		
CD$_4$ C$_2$H$_6$	2.99	1.75	C$_2$H$_6$ > CD$_4$	104.7 98.0
CH$_4$ C$_2$D$_6$	0.56	0.84	C$_2$H$_6$ > CH$_4$	103.8 98.9
CD$_4$ C$_3$H$_8$	3.99	2.21	C$_3$H$_8$ > CD$_4$	104.7 96.7
CH$_4$ C$_3$D$_8$	0.36	0.57	C$_2$D$_8$ > CH$_4$	103.8 97.6
C$_2$D$_6$ C$_3$H$_8$	2.13	1.76	C$_3$H$_8$ > C$_2$D$_6$	98.6 96.7
C$_2$H$_6$ C$_3$D$_8$	0.83	0.87	C$_3$D$_8$ $\simeq$ C$_2$H$_6$	98.0 97.6

[a] Extrapolated values. [b] J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966). The C–D bond strength is taken to be 0.9 kcal greater than that of C–H: S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 676.

energies. Furthermore, the magnitude of the effect of moderation is proportional to the difference in bond

(6) D. Seewald and R. Wolfgang, *J. Chem. Phys.*, **47**, 143 (1967).

(7) R. T. K. Baker, unpublished results.

(8) We implicitly assume here that, if more atoms survive to reach the lower hot-energy range, there will be relatively more collisions at those energies. Hence, moderation would increase the ratio of low-energy to high-energy hot reaction. There is, however, one extraordinary set of circumstances where the reverse would be true. The number of collisions in a given energy range is determined not only by the number of atoms which reach it, but by their energy loss per collision. Consider now the ratio of mean logarithmic energy loss per collision with reactant and with moderator, α(reactant)/α(moderator).[5] If with decreasing energy this ratio is approximately constant, or increases, or even decreases somewhat, then dilution with moderator will increase the relative number of low-energy collisions. But if it decreases sharply, then the relative number of low-energy collisions will actually decrease. Such a situation would reverse the conclusions we now draw from our data. Consideration of the nature of energy-loss collisions implies that this is quite unlikely. Furthermore, experiments on CD$_4$–C$_2$H$_6$ mixtures yield qualitatively similar results if CF$_4$ is substituted as a moderator for Ne. Energy-loss mechanisms in collisions with CF$_4$ are similar to those with CD$_4$ and C$_2$H$_6$, with internal as well as translational modes being involved. Hence, in this case, it seems even more implausible that α(reactant)/α(moderator) would vary enough with energy to reverse our conclusions. Nevertheless, this possibility cannot be completely excluded, and our conclusions must be considered to rest on a plausible, but as yet unproven, assumption.