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 elsewhere.[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_2H_6. It appears that abstraction from C_2H_6 occurs at a higher mean energy than from CD_4.[8] Since the C–H bond strength of C_2H_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 energies. Furthermore, the magnitude of the effect of moderation is proportional to the difference in bond

Table I

Reaction mixture	HT/DT yield ratio No moderation	HT/DT yield ratio 100% moderation[a]	Mean rel abstr energy	Bond energy,[b] kcal
CD_4 C_2H_6	2.99	1.75	$C_2H_6 > CD_4$	104.7 98.0
CH_4 C_2D_6	0.56	0.84	$C_2H_6 > CH_4$	103.8 98.9
CD_4 C_3H_8	3.99	2.21	$C_3H_8 > CD_4$	104.7 96.7
CH_4 C_3D_8	0.36	0.57	$C_2D_8 > CH_4$	103.8 97.6
C_2D_6 C_3H_8	2.13	1.76	$C_3H_8 > C_2D_6$	98.6 96.7
C_2H_6 C_3D_8	0.83	0.87	$C_3D_8 \simeq C_2H_6$	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.

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(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, $\alpha(\text{reactant})/\alpha(\text{moderator})$.[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_2H_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_2H_6, with internal as well as translational modes being involved. Hence, in this case, it seems even more implausible that $\alpha(\text{reactant})/\alpha(\text{moderator})$ 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.

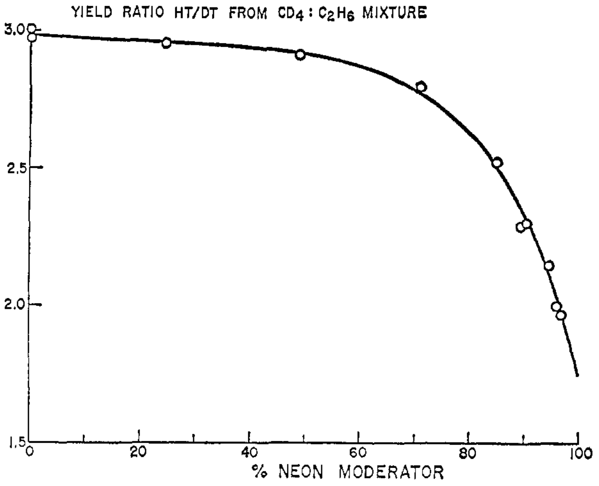

Figure 1. Variation of HT/DT ratio from recoil tritium reaction with equimolar CD_4–C_2H_6 mixture, as a function of moderation.

energies. In fact, by considering these magnitudes, it becomes evident that the mean energy of abstraction changes in the sequence CH_4, C_2H_6, C_3H_8 and also CD_4, C_2D_6, and C_3D_8. This is also the order of decreasing bond energies.

These findings are consistent with our result that abstraction by recoil tritium occurs, on the average, at higher energies than does displacement.[6,7]

$$T + RH \longrightarrow RT + H$$

They indicate further that the mean energy of abstraction increases with decreasing bond strengths. High-energy stripping reactions of neutral hot atoms were first postulated to account for the effect of bond strengths on hydrogen yields.[5] Confirmation of the consequent prediction[6] that abstraction can occur at high mean energies, and that it is this high-energy mode that seems to be enhanced when the hydrogen bond in the reactant is weakened,[8] provides strong support for the existence and importance of such a high-energy stripping mechanism.

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The Synthesis and Characterization of Poly d(I-C)·Poly d(I-C)[1]

Sir:

High molecular weight deoxyribopolynucleotides containing repeating base sequences are of interest as model compounds for a variety of chemical and biological studies. A series of such polymers has been recently synthesized by a combination of chemical and enzymatic techniques.[2] The copolymer which contains repeating adenylic and thymidylic acid units has been well characterized[3] and has been the subject of considerable investigation;[4] however, the polymer which contains repeating deoxyriboinosinic and deoxyribocytidylic acid units, poly d(I-C)·poly d(I-C),[5] has eluded preparation to date. Similarly, the synthesis of poly d(G-C)·poly d(G-C) has not been reported.

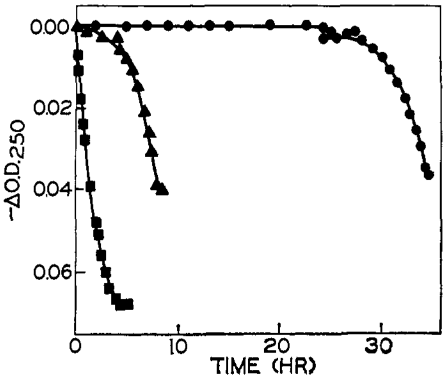

Figure 1. Polymer synthesis by the *Micrococcus lysodeikticus* DNA polymerase in the presence of dITP and dCTP. The reaction mixtures were prepared as described in the text. The development of hypochromicity at 250 mμ was used to follow polymer formation; ● indicates unprimed reaction in Tris–HCl buffer (pH 8.0), ▲ indicates poly dI·poly dC primed reaction in Tris–HCl buffer (pH 8.0), and ■ indicates poly dI·poly dC primed reaction in phosphate buffer (pH 7.3). Other details are described in the text.

We wish to report the synthesis of poly d(I-C)·poly d(I-C), a high molecular weight, helical deoxyribopolynucleotide containing strictly alternating deoxyribocytidylic acid and deoxyriboinosinic acid units. The polymer has been characterized by the following techniques: nearest neighbor frequency analyses, sedimentation velocity studies in both neutral and alkaline salt solutions, cesium chloride and cesium sulfate equilibrium buoyant density studies in both neutral and alkaline solutions, ultraviolet spectral data, and ultraviolet absorbance–temperature profiles. The physical properties of poly d(I-C)·poly d(I-C) are markedly different from the physical properties of poly dI·poly dC.[6]

Poly d(I-C)·poly d(I-C) was synthesized as a *de novo* product by the *Micrococcus lysodeikticus* DNA polymerase in the presence of dITP and dCTP (Figure 1). After a lag period of many hours the reaction exhibited exponential kinetics and was complete in 34.5 hr; the extent of hypochromicity developed at 250 mμ was 16%, which corresponded to the incorpora-

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(1) The authors wish to express their appreciation to the National Science Foundation, the Life Insurance Medical Research Foundation, and the Wisconsin Alumni Research Foundation for their generous support of this investigation.

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