Journal of Photochemistry
Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Preliminary Note

Halogen abstraction by hot hydrogen atoms

G. A. OLDERSHAW and A. SMITH
Department of Chemistry, University of Hull, Hull HU6 7RX (Gt. Britain)
(Received January 8, 1973)

Hydrogen atoms generated by ultra-violet photolysis of the hydrogen halides possess considerable translational energy and are significantly more reactive than thermalized species[1]. Most previous work[2-6] with such atoms has been concerned with hydrogen abstraction, and reactions involving heavier atoms have received little attention, the only processes studied being the abstraction of O from N_2O[7,8] and CO_2[7,9], the abstraction of N from N_2O[7,9] and the abstraction of S from OCS[10]. We report here the observation of abstraction of halogen atoms from methyl chloride and methyl bromide by hot hydrogen atoms produced in the photolysis of hydrogen iodide.

Photolysis at 298 nm of hydrogen iodide mixed with methyl chloride or bromide yielded hydrogen and methane as the only products volatile at 113 K. Since absorption by CH_3Cl and CH_3Br is negligible at this wavelength, we attribute the formation of CH_4 mainly to the hot abstraction reaction:

$$H^* + CH_3X \rightarrow HX + CH_3 \quad (1)$$

If H* is a hydrogen atom with energy above the threshold for reaction (1), H is one with less than this energy, and M is any added unreactive gas, the reaction scheme is as follows:

$$HI + h\nu \rightarrow H^* + I$$
$$H^* + CH_3X \rightarrow HX + CH_3 \quad (1)$$
$$H^* + CH_3X \rightarrow X + CH_4 \quad (2)$$
$$H^* + CH_3X \rightarrow H_2 + CH_2X \quad (3)$$
$$H^* + CH_3X \rightarrow H + CH_3X \quad (4)$$
$$H^* + HI \rightarrow H_2 + I \quad (5)$$
$$H^* + HI \rightarrow H + HI \quad (6)$$
$$H^* + M \rightarrow H + M \quad (7)$$
$$H + HI \rightarrow H_2 + I \quad (8)$$
$$CH_3 + HI \rightarrow CH_4 + I \quad (9)$$

Hydrogen atoms are generated with a translational energy of 109 kJ mol^{-1} and may subsequently react via processes (1), (2), (3) and (5) or lose energy in the multistage thermalization processes (4), (6) and (7). If it is assumed that all methyl radicals and deactivated hydrogen atoms react with HI, the composition of the products is determined by competition between the hot reactions and the moderation processes, and

$$\frac{[H_2]}{[CH_4]} = \frac{(k_3 + k_4)}{(k_1 + k_2)} + \frac{(k_5 + k_6)}{(k_1 + k_2)} \frac{[HI]}{[CH_3X]} + \frac{k_7}{(k_1 + k_2)} \frac{[M]}{[CH_3X]} \tag{10}$$

Possible scavenging of H and CH_3 by small quantities of iodine produced during the photolysis is neglected since the relative rates of reaction with I_2 and with HI are similar for H and for CH_3[11]. Mass spectrometric analysis of the products of several runs gave the results shown in Fig. 1. In the absence of added moderators, the anticipated linear relationships between $[H_2]/[CH_4]$ and $[HI]/[CH_3X]$, which are characteristic of hot reactions[2], are observed.

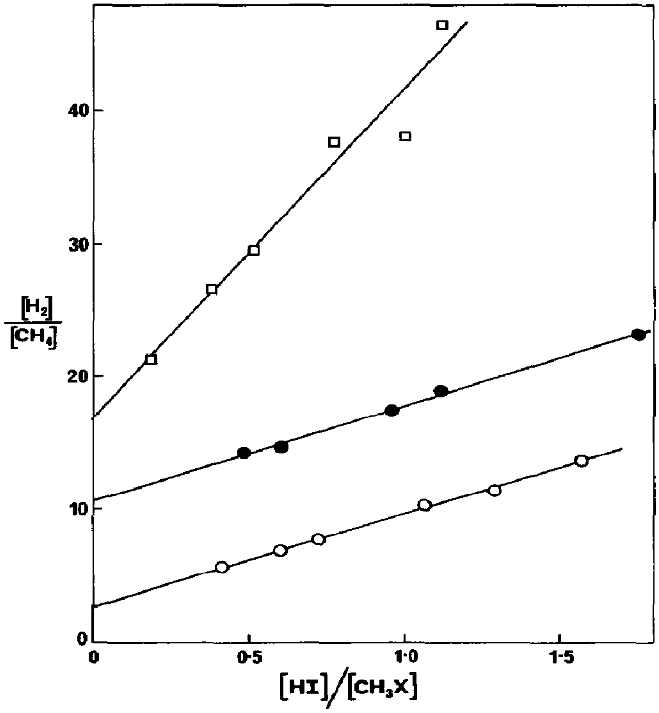

Fig. 1. Product ratio as a function of mixture composition. □, CH_3Cl + HI; ○, CH_3Br + HI; ●, CH_3Br + HI + CO_2, with $[CO_2]/[CH_3Br]$ = 4.82.

H* reacts much more readily with CH_3Br than with CH_3Cl, as is evident from the greater production of methane in the CH_3Br/HI runs. The proportion of hydrogen atoms which would react with CH_3X in processes (1) and (2) in the absence of HI is $(k_1 + k_2)/(k_1 + k_2 + k_3 + k_4)$; this fraction can be calculated from the intercepts of the plots shown in Fig. 1 and is equal to 0.27 for CH_3Br and 0.056 for CH_3Cl. Both the abstraction and substitution reactions (1) and (2) ultimately produce methane and their relative importance cannot be established from the product composition. Analogy with the substitution of T for D or H[12,13], however, suggests that reaction (1) predominates at the low energies used here, although reaction (2) is significant for recoil tritium atoms[14,15].

The proportion of methane in the products of the CH_3Br/HI runs is reduced by the addition of carbon dioxide. This confirms that CH_4 is produced *via* a hot reaction, since the effect of CO_2 is to remove energy from H* in moderating collisions. Figure 1 shows results obtained for a fixed ratio (4.82) of CO_2 to CH_3Br. The slope of the plot (7.2 ± 0.3) is equal to that obtained in the absence of moderators (7.0 ± 0.2), in agreement with eqn. (10), and the value of $k_7/(k_3 + k_4)$, derived from the intercepts of the two plots, is 0.61. Since k_3 is probably small compared with k_4, this shows that, despite its greater mass, CH_3Br is a more effective moderator of H* than is CO_2.

A. S. thanks the Science Research Council for a maintenance award.

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