1.05 (3 H, *s*), 1.27 (3 H, *d*, $J = 6.5$ Hz), 1.90 (3 H, *d*, $J = \sim 1$ Hz), 2.32 (2 H, *q* AB, $J = 17$ Hz), 2.55–3.00 (2 H, *m*, OH), 4.37 (1 H, br. *m*), 5.80 (3 H, narrow *m*).

$C_{13}H_{20}O_3$ (224.30) Calc. C 69.61 H 8.99% Found C 69.46 H 8.81%

4. *Blumenol C* (**6**). This compound was isolated from crude ketone **4** by preparative GLC. (see *fig.*). IR. (neat): $\nu = 1120, 1255, 1295, 1380, 1650, 3450$ cm^{-1}; MS.: $M^+ = 210$, base peak *m/e* 43, other prominent peaks at *m/e* 177, 150, 135, 123, 108, 95, 93, 69; NMR. ($CDCl_3$): $\delta = 1.00$ (3 H, *s*), 1.05 (3 H, *s*), 1.18 (3 H, *d*, $J = 6$ Hz), 1.98 (3 H, *d*, $J = \sim 1$ Hz), 2.20 (2 H, *q*, *AB*, $J = 17$ Hz), 1.3–2.2 (5 H, *m*), 3.75 (2 H, *m* + *s*), 5.78 (1 H, *s*).

5. *Allenic ketol* **7**. This compound was also isolated by preparative GLC. (see *fig.*) and exhibited the following properties: IR. (neat): $\nu = 925, 1075, 1100, 1115, 1265, 1360, 1375, 1595, 1650, 1930, 3430$ cm^{-1}; MS.: $M^+ = 206$, base peak *m/e* 147, other prominent ions at *m/e* 162, 106, 45, 43; NMR. ($CDCl_3$): $\delta = 1.17$ (6 H, *s*), 1.35 (3 H, *d*, $J = 6$ Hz), 2.00 (3 H, *s*), 2.35 (2 H, *s*), 3.25 (1 H, br. *s*, OH), 4.45 (1 H, *m*), 5.80 (2 H, *s* + *d*).

6. *3,3,5-Trimethyl-4-(3-hydroxybutylidene)-cyclohexan-1-one* (**8**). Like the two preceding compounds, this substance was isolated by preparative GLC. of crude ketone **4** (see *fig.*). IR. (neat): $\nu = 935, 1040, 1070, 1110, 1235, 1370, 1450, 1700, 3450$ cm^{-1}; MS.: $M^+ = 210$, base peak *m/e* 109, other prominent fragments at *m/e* 166, 151, 82, 81, 69, 67, 45; NMR. (CCl_4): $\delta = 1.16$ (12 H, *m*), 1.9–2.7 (7 H, *m*), 3.20 (1 H, br. *s*), 3.75 (1 H, br. *m*), 5.47 (1 H, *t*, $J = 6.5$ Hz).

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227. The Wall Effect on Hydrogen Formation in the Vapour-Phase Radiolysis of c-C_6D_{12} and n-C_7D_{16}

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(7. VIII. 74)

Summary. Vapour-phase radiolysis of c-C_6D_{12} and n-C_7D_{16} leads to a relatively large HD yield, up to ~20% of the total hydrogen, which cannot be accounted for by incomplete deuteration of c-C_6D_{12} and n-C_7D_{16}. In order to elucidate the mechanism of the HD formation, we have examined the effect of additives and of physical conditions on the HD yield. By coating the vessel with a layer of Aquadag the HD yield is greatly decreased without appreciable variation of the total hydrogen yield. The HD yield from nontreated vessels also decreases remarkably with increasing total dose; it is increased upon the addition of traces of water; and is less affected by small amounts of c-C_6H_{12}. The addition of SF_6 selectively reduces the HD yield. These experimental results lead us to conclude that inert hydrocarbon ions react by proton transfer with water desorbed from the vessel wall to give hydronium ions which yield HD on subsequent neutralization.

1. Introduction. – In the vapour-phase radiolysis of n-C_7H_{16}/n-C_7D_{16}-mixtures, we noticed a relatively large yield of HD from pure n-C_7D_{16} [1]. A similar yield of HD of about 30% of G (total hydrogen) has also been measured in the gas-phase radiolysis of C_3D_8 [2] [3]. This seems to be characteristic of the gas-phase radiolysis of paraffinic deuterated hydrocarbons, because it is not observed in the liquid phase radiolysis of the same hydrocarbons [4] [5]. This phenomena perturbs the kinetic treatment of the hydrogen formation from protiated and perdeuterated hydrocarbon mixtures. *Bone et al.* [2] have ascribed it to the occurrence of a neutralization reaction on the vessel wall. However there have been no systematic investigations of the HD formation from perdeuterated hydrocarbons. We attempt in this publication to elucidate the mechanism of the HD formation from c-C_6D_{12} and n-C_7D_{16}.

2. Experimental Part. – 2.1. *Materials.* The deuterated compounds were produced in an automatic exchange apparatus [6] and purified by distillation and gas-chromatography [4]. The isotopic purity of these compounds was determined to be higher than 99.6 at. %. c-C_6H_{12} (*Phillips* research grade), sulfur hexafluoride (*Air Liquide*), and the distilled water were degassed by several freezing thawing cycles prior to use. Aquadag (*Acheson Colloid Co.,*) was used after dilution with water (water/Aquadag = $^1/_4$).

2.2. *Sample preparation.* Cylindrical Pyrex vessels of *ca.* 9 cm length, 4.5 cm diameter and 140 cm³ volume were used. They were throughly flamed on the vacuum line before introducing the samples. This procedure, however, does not guarantee the complete elimination of water from the vessel wall. In some experiments, the vessels were coated internally with a layer of Aquadag (graphite). They were heated for 6 h at 550° in air to eliminate any trace of solvent. An attempt has also been made to exchange the hydrogen on the wall of the vessel by deuterium by washing the vessel with D_2O, and running a *Tesla* coil over the wall in the presence of D_2O vapour. The samples to be irradiated were degassed and transferred to the irradiation vessels *in vacuo* at –196°. Additives were transferred from a calibrated volume after measuring the pressure and temperature.

2.3. *Irradiation and analysis.* The samples were enclosed in an electric furnace and irradiated in a ^{60}Co-source. Irradiation temperatures were 120 ± 3° for c-C_6D_{12} and 80 ± 2° for n-C_7D_{16}. All samples were irradiated to 2 Mrad (except for the dose-dependence study) at a dose rate of 1.0 Mrad/h. The analytical procedures were essentially the same as those described previously [7].

3. Results. – We have first checked that irradiation of empty vessels gave no significant amount of products under the conditions employed in the present study. Fig. 1a shows the dose dependence of G-values and the isotopic composition of the hydrogen formed in the vapour-phase radiolysis of deuterated cyclohexane at 100 and 1000 Torr. A decrease in the percentage of HD with increasing dose is accompanied by a corresponding increase in D_2. The results indicate that impurities which are precursors of HD are consumed by prolonged irradiation. Fig. 1b shows the dose dependence of the HD and H_2 production from c-C_6D_{12}. When the samples were irradiated at 1000 Torr, the HD yield attains a constant value at the highest dose used. Fig. 2a and table 1 show the pressure effect on the H_2, HD, and D_2 production. Vessels with and without Aquadag treatment were used in this experiment. G(HD) for treated vessels is always less than that for untreated vessel, although the results from untreated vessels show some scatter. *Bone et al.* [2] also observed that G(HD)

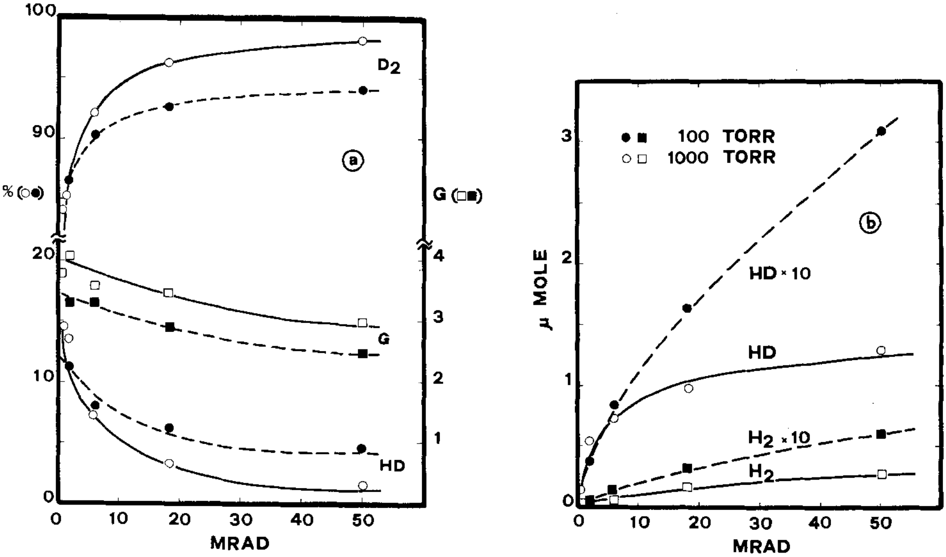

Fig. 1. *The dose dependence of hydrogen production in* c-C_6D_{12} *at 120°.* Filled symbols: 100 Torr. Empty symbols: 1000 Torr

Table 1. *The pressure dependence:* $G\ (Y) = a_0 + a_1 \cdot 10^{-5} \cdot P$ *Torr for the hydrogen production* (120°, 2 Mrad)

Y	SF_6	without aquadag		with aquadag	
	mol %	a_0	a_1	a_0	a_1
H_2	0	0.06 ± .01	− 2 ± 1	0.024 ± .008	0 ± 1
HD	0	0.62 ± .12	−20 ± 12	0.24 ± .03	− 2 ± 4
D_2	0	3.28 ± .09	15 ± 10	3,62 ± .14	−17 ± 17
H_2	0.3	0.018 ± .004	−0.5 ± .5	0.007 ± .002	−0.2 ± .3
HD	0.3	0.075 ± .003	−0.7 ± .3	0.072 ± .008	−0.5 ± 1.0
D_2	0.3	2.82 ± .01	+7 ± 1	2.66 ± .01	+10 ± 1

from C_3D_8 decreased to a great extent by coating the vessel with a layer of Aquadag. The addition of 0.3% SF_6 to *c*-C_6D_{12} decreases G(total hydrogen) by 0.9 and G(HD) to negligible amount as shown in Fig. 2b. In the presence of the electron scavenger SF_6, both treated and nontreated vessels gave almost the same G(HD) irrespective of pressure. Fig. 3a shows the effect of the addition of traces of water. G(HD) increases appreciably, suggesting that water is involved in the HD formation.

Fig. 3b shows the effect of *c*-C_6H_{12} on the hydrogen production from *c*-C_6D_{12}. In this case, G(HD) is little affected by the addition of small amounts of *c*-C_6H_{12}. In Fig. 4, the G-value of H_2, HD and D_2 is plotted as a function of the surface to volume ratio (S/V). The surface area is increased by putting Pyrex glass tubes in the vessel. An increase in S/V from 1.1 up to 3.5 cm^{-1} caused no appreciable increase in G(HD). Table 2 summarizes some experimental results. They are very similar for *c*-C_6D_{12} and

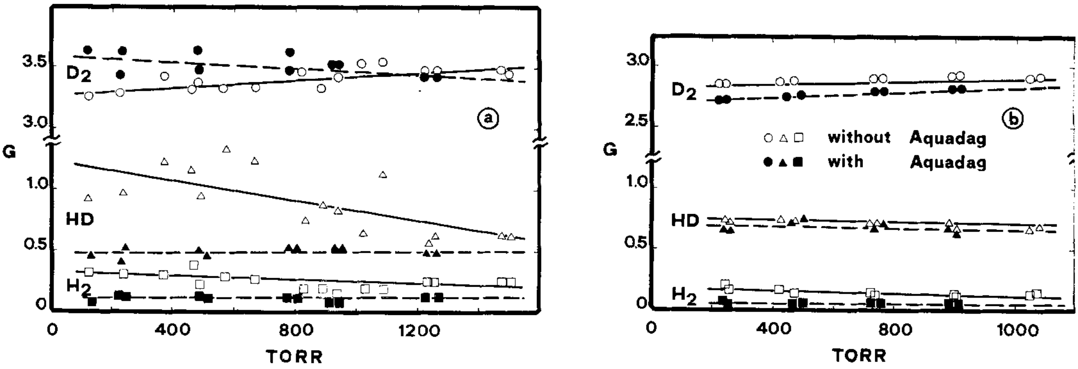

Fig. 2. *The pressure dependence of hydrogen production in* c-C_6D_{12} *at 120° and 2 Mrad.* Filled symbols: surface treated with aquadag. Empty symbols: untreated surface. a: no additive; G(HD) × 2; G(H_2) × 5. b: 0.3 mol % SF_6 added; G(HD) × 10, G(H_2) × 10

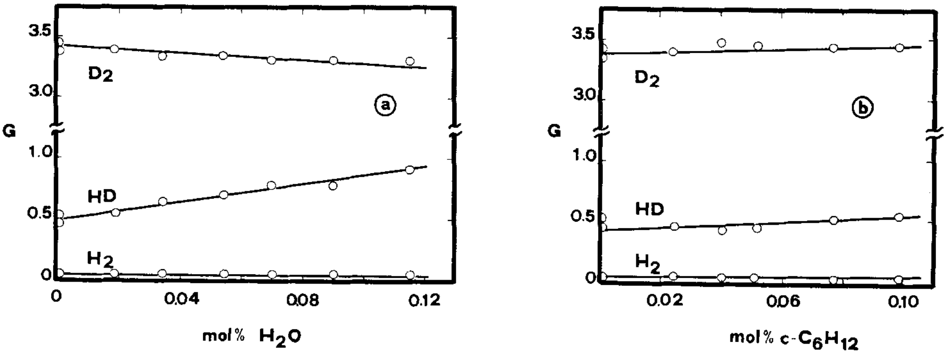

Fig. 3. *The effect of traces of water (a) and cyclohexane (b) on H_2- and HD-production in cyclohexane at 120°, 500 Torr and 2 Mrad*

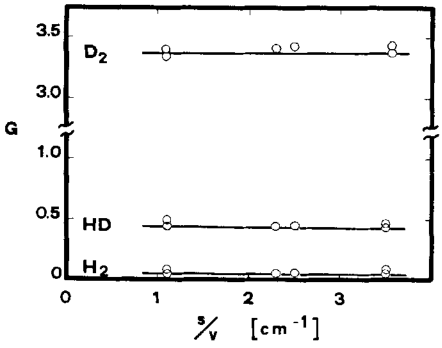

Fig. 4. *The dependence of hydrogen production in C_6D_{12} on the surface to volume ratio S/V at 120°, 500 Torr and 2 Mrad*

Table 2. *Wall effect on the hydrogen formation in the vapour-phase radiolysis of* n-C_7D_{16}[a]) *and* c-C_6D_{12}[b])

n-C_7D_{16}				*c*-C_6D_{12}				Surface	Additive
G(total hydrogen)	%H_2	%HD	%D_2	G(total hydrogen)	%H_2	%HD	%D_2	treatment	
3.70 ± 0.15[c])	2.3	18.4	79.3	3.80 ± 0.15	1.3	14.3	84.4	None	None
3.65 ± 0.15	0.9	5.0	94.1	3.80 ± 0.15	0.7	6.1	93.2	(A)	None
2.70 ± 0.15	1.2	0.6	98.2	2.90 ± 0.15	0.5	2.5	97.0	None	0.3% SF_6
2.70 ± 0.15	0.5	0.6	98.9	2.80 ± 0.15	0.2	2.6	97,2	(A)	0.3% SF_6
3.80 ± 0.15	2.2	11.2	86.6					(B)	None

[a]) Dose; 2.0 Mrad; pressure: *ca.* 220 Torr; irradiation temperature: 80°.

[b]) Dose; 2.0 Mrad; pressure; *ca.* 500 Torr; irradiation temperature: 120°.

[c]) The error given corresponds to the standard error of several replica.

(A) The vessels were coated with a layer of Aquadag.

(B) The vessels were first washed three or more times with D_2O. Then, they were flashed with a *Tesla* coil over the surface on the vacuum line in the presence of D_2O vapour.

n-C_7D_{16}. One notes that a HD yield of 20% of the total hydrogen is replaced by an equivalent amount of D_2 by coating the vessel with an Aquadag layer. Selective reduction of HD is also observed upon the addition of SF_6. In the presence of SF_6 the surface treatment has almost no effect on G(HD). A decrease in G(HD) when irradiating *n*-C_7D_{16} is also observed upon exchanging H_2O on the wall by D_2O prior to filling the vessel.

4. Discussion. – We propose the following reaction scheme to interpret our experimental results obtained with *c*-C_6D_{12}:

$$c\text{-}C_6D_{12} \rightsquigarrow c\text{-}C_6D_{12}^{*} \tag{1}$$

$$\rightsquigarrow RD^{+} + e^{-} \tag{2}$$

$$c\text{-}C_6D_{12}^{*} \longrightarrow D,\ D_2,\ P \tag{3}$$

$$RD^{+} + e^{-} \longrightarrow D,\ D_2,\ P' \tag{4}$$

$$RD^{+} + H_2O\ (\text{vapour}) \longrightarrow H_2DO^{+} + R \tag{5}$$

$$H_2O\ (\text{wall}) \rightleftharpoons H_2O\ (\text{vapour}) \tag{6}$$

$$H_2DO^{+} + e^{-} \longrightarrow H + HDO \tag{7}$$

$$\longrightarrow D + H_2O \tag{8}$$

$$H + c\text{-}C_6D_{12} \longrightarrow HD + c\text{-}C_6D_{11} \tag{9}$$

where RD^+ represents any long-lived ion. It may be *c*-$C_6D_{12}^+$, *c*-$C_6D_{11}^+$, or a fragment ion thereof. P and P′ are products.

Dose effect. The HD yield from *c*-C_6D_{12} decreases with increasing dose as shown in Fig. 1a. This suggests that the impurity which is the precursor of the HD is consumed by prolonged irradiation, even though the interpretation of the dose effect is not straightforward because of the occurrence of complex secondary reactions at high doses. We consider the impurity to be water which desorbs from the wall of the vessel during irradiation. A desorbed water molecule accepts a proton in reaction (5) and leads eventually to HD formation by reactions (7) and (9). This is corroborated by other observations that will be discussed later on. This sequence is in competition with (4) and thus does not alter substantially G (total hydrogen). Other possible sources of water can be ruled out. The solubility of water in $c\text{-}C_6D_{12}$ is too small to form an important source of water. Further, if the dissolved water were the sole source of water, the HD yield obtained at the high dose should be directly proportional to the quantity of the sample *i.e.* the pressure of $c\text{-}C_6D_{12}$. As seen in Fig. 1b, this is not the case. Irradiation at 1000 Torr approaches a plateau of approx. 1.2 μmol HD at 50 Mrad, whereas irradiation at 100 Torr gives a HD yield at 50 Mrad which is still increasing with increasing dose. The dose dependence can be explained by the disappearance of H_2O by deuteration (reaction (7)) and/or by reacting with secondary products of radiation. On the other hand, if water absorbed on the wall of the vessel were the unique source of water, the HD yield obtained at high dose should be independent of the quantity of the sample. This is probably true since the HD production from 100 Torr $c\text{-}C_6D_{12}$ seems to reach that from 1000 Torr $c\text{-}C_6D_{12}$ at still higher doses. The following consideration suggests that the contribution of incompletely deuterated cyclohexane ($c\text{-}C_6D_{11}H$) to the HD formation is unimportant. The HD yield from 1000 Torr $c\text{-}C_6D_{12}$ reachs at a plateau value at 50 Mrad where approximately 1% of the sample has been decomposed. On the other hand, since our sample contains *ca.* 5% $C_6D_{11}H$, we still have a large amount of $c\text{-}C_6D_{11}H$ left after a dose of 50 Mrad, even if we assume a selective decomposition of $c\text{-}C_6D_{11}H$ to take place. Therefore, if $c\text{-}C_6D_{11}H$ were the main source of the HD, we could not explain the approximate saturation of the HD yield at 50 Mrad.

Effect of Surface Treatment. When the wall of the vessel is coated with a layer of Aquadag, a remarkable decrease in the percentage HD formed is observed and shown in Fig. 2a. We consider that the difference encountered with the untreated vessel is due to the occurence of reactions (5)–(9). A wall coated with a layer of graphite will prevent the diffusion of water adsorbed on Pyrex into the volume during irradiation. We infer that the water concentration on the Aquadag surface is smaller than on Pyrex, giving the decreased HD yield for the treated vessels.

We can roughly estimate the concentration of H_2O at which RD^+ reacts with H_2O with a probability of 0.5, *i.e.* rate R_4 = rate R_5. In this case we have

$$R_4/R_5 = 1 = k_4 \cdot [RD^+] \cdot [e]/k_5\,[RD^+] \cdot [H_2O] = k_4[e]/k_5[H_2O]$$

or

$$[H_2O]_{R_4=R_5} = k_4[e]/k_5$$

With the steady state approximation:

$$d[e]/dt = I - k_4[e]\,[RD^+] - (k_7 + k_8)\,[e]\,[H_2DO^+] = 0$$

and the assumption that $k_4 = k_7 + k_8$ and $[e] = [RD^+] + [H_2DO^+]$ (charge conservation) we obtain

$$[e] = (I/k_4)^{1/2}$$

and thus for the concentration of water:

$$[H_2O]_{R_4=R_5} = (k_4\,I)^{1/2}/k_5. \qquad (A)$$

I is the rate of ion pair production, being $23 \cdot 10^{10}$ ion pair/cm$^3 \cdot$ s at 120° and 100 Torr.

Neutralization reactions such as (4) and (7), have rate constants of the order of 10^{-6} cm^3/ion · s [8]. In a mass spectrometric study the rate constant for the proton transfer reaction (5) has been determined to be 5.6×10^{-11} cm^3/molecule · s [9]. Substituting these values into eq. (A) gives $[H_2O] = 8.6 \times 10^{12}$ molecule/cm^3 which corresponds to $\sim$0.0004% H_2O at 100 Torr and 120°.

The HD yield from n-C_7D_{16} is decreased considerably upon exchanging H_2O on the wall of the vessel by D_2O (Table 2). In this case, D_2O desorbs from the wall and reacts with RD^+ to give D_3O^+, which subsequently gives a D atom upon neutralization. The incomplete suppression of HD reflects the difficulty of completely exchanging H_2O by D_2O. These results provide additional evidence that H_2O adsorbed on the wall may be the precursor of the HD.

Effect of Water. The observation that the HD yield is sensitive to the addition of small amounts of water strengthens our opinion that water traces are involved in HD formation (Fig. 3a). The rate of reaction (5) should increase with increasing water concentration. Thus the increase in the HD yield upon the addition of water traces is in good agreement with our reaction scheme. The H_2 yield is barely modified by the addition of H_2O. This is reasonable because the hydronium ion of rct. (7) and (8) is known to give atomic hydrogen (deuterium) and no molecular hydrogen upon neutralization in the radiolysis of water vapour [10].

Effect of SF_6. The addition of 0.3% SF_6 to c-C_6D_{12} selectively decreases the HD yield from untreated vessels to negligible values as seen in Fig. 2b. This indicates that a neutralization reaction is involved in the HD formation, since SF_6 is an electron scavenger [11]. Reactions (10) and (11) will occur in the presence of SF_6:

$$SF_6 + e^- \longrightarrow X^- \tag{10}$$

$$H_2DO^+ + X^- \longrightarrow \text{no hydrogen.} \tag{11}$$

Even if reaction (5) occurs in the presence of SF_6, H_2DO^+ gives no hydrogen upon neutralization so that the HD yield from untreated vessels decreases upon addition of SF_6. We also expect no effect of the surface treatment on the G(HD) in the presence of SF_6, by virtue of the occurrence of reaction (11). In fact, in the presence of SF_6, G(HD) from untreated vessels is almost same as that from treated ones.

Effect of c-C_6H_{12}. Since we cannot *a priori* rule out the possibility that some organic protiated compounds desorb from the wall leading to HD, we have examined the effect of small concentrations of c-C_6H_{12} on the HD yield. Increase in the HD yield upon addition of c-C_6H_{12} is always smaller than that of H_2O as seen in Fig. 3. However, the change in the HD yield caused by the addition of 0.1% c-C_6H_{12} is still large, being calculated to be 0.09 from a regression line. If we assume that the c-C_6H_{12} added competes simply with c-C_6D_{12} for the thermal D atoms produced from c-C_6D_{12} by reaction (9) the increment of G(HD) can be estimated to be 0.03 at 0.1% c-C_6H_{12} assuming a kinetic isotope effect k_H/k_D of 13 and a G-value of thermal D atoms from c-C_6D_{12} of 2 (4). Thus the increase in the HD yield upon addition of c-C_6H_{12} cannot be accounted for by only thermal D atom scavenging by c-C_6H_{12}. We may then deduce the occurrence of an energy (or charge) transfer from c-C_6D_{12} to c-C_6H_{12} leading to an enhanced HD yield.

Effect of S/V. Fig. 4 shows that an increase in the surface to volume ratio from 1.1 to 3.5 causes no significant increase in the HD yield. This probably means that the concentration of water in the gas phase does not vary with S/V. We can try to estimate the concentration of water in the gas phase as a function of S/V by assuming that the total number of water molecules in the system is equal to the surface area of the system [S] multiplied by the water concentration per unit surface area [c] before irradiation, eq. (B) and that there is an equilibrium between water desorbed from and adsorbed on the wall, eq. (C).

$$\mathrm{n} + \mathrm{N} = \mathrm{cS} \tag{B}$$

$$(\mathrm{n/V} \,/\, \mathrm{N/S}) = \mathrm{K} \tag{C}$$

where N is total number of water molecules adsorbed on the surface [molecule], n, total number of water molecules in the gas phase [molecule], V, volume of the vessel [cm^3], S, surface area of the system [cm^2], c, the water concentration per unit surface area before irradiation [$\mathrm{molecules/cm}^2$] and K, equilibrium constant [cm^{-1}]. From eq. (B) and (C), we obtain the concentration of water per unit volume:

$$\mathrm{n/V} = Kc/(1 + K\mathrm{V/S}). \tag{D}$$

Experimental results suggest that n/V does not vary with S/V. We can expect such a condition if $1 \gg K\mathrm{V/S}$ or $\mathrm{S/V} \gg K$. In our case, the minimum S/V is 1.1 so that $K \ll 1\ \mathrm{cm}^{-1}$. This means that a small fraction of the water adsorbed on the wall desorbs during irradiation.

Another viewpoint also leads to an estimate of the equilibrium constant $K \ll 1$: in our reaction scheme one H_2O molecule can eventually give rise to two HD molecules, then one half of the plateau value of the HD yield (0.6 μmol at 1000 Torr c-C_6D_{12}) is taken to represent the total number of water molecules in the system, *i.e.* n + N. On the other hand, the concentration of water per unit volume, n/V, has been already estimated to be $\sim 8.6 \times 10^{12}$ $\mathrm{molecules/cm}^3$. Substituting these values and surface area (150 cm^2), of the vessel into eq. (C) gives $K = 3.6 \times 10^{-3}\ \mathrm{cm}^{-1}$, which is compatible with our inference that $K \ll 1$.

The discussion presented above holds also for the HD formation from n-C_7D_{16} without any significant modification.

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