Notes

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	UNIT C	ELL DIMENSIONS (OF RARE EARTH I	DISILICIDE POLYMO	ORPHS"	
	Temp.,	Low temp. form ^{a}			High temp. forma	
Compound	°C.	a (Å.)	b (Å.)	c (Å.)	a (Å.)	c (Å.)
$PrSi_2$	-130	4.23	4.20	13.68	(4.20)	(13.76)
$SmSi_2$	470	(4.105)	(4.035)	(13, 46)	4.08	13.51
$GdSi_2$	460	(4.09)	(4.01)	(13.44)	4.10	13.61
DySi_2	585	(4.04)	(3.95)	(13.33)	4.03	13.38
YSi_2	545	(4.04)	(3.95)	(13.33)	4.04	13 , 42
Parentheses inc	tigata room tamp	areture form				

TABLE II

^a Parentheses indicate room temperature form.

transformation similar to that noted above occurs in the cases of these compounds at still lower temperatures. Lattice dimensions of the polymorphs which could be measured with reasonable precision are shown in Table II.

THE REACTION OF PERFLUORO-n-PROPYL **RADICALS WITH CYCLOHEXANE IN THE** GAS PHASE¹

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Recently Giacometti and Steacie² have measured the rates of reaction of C_3F_7 radicals with methane and ethane. They obtained $k_1/k_2^{1/2} = 9.7 \times 10^3$ exp[- (9.5 ± 0.5) × 10³/RT] (mole/cc.)^{-1/2} sec.^{-1/2} for methane, and $k_1/k_2^{1/2} = 1.7 \times 10^5$ exp[- (9.2 ± 0.5) × 10³/RT] (mole/cc.)^{-1/2} sec.^{-1/2} for ethane, where subscript 1 refers to the hydrogen abstraction reaction and subscript 2 to the radical recombination reaction.

It is seen that these results are in contradistinction to similar CH_3 and CF_3 radical systems where the difference in rate constants is reflected almost entirely in the activation energies of the processes, the pre-exponential factors being approximately constant for either series. Further, in methyl radical systems the activation energies of the hydrogen abstraction reactions exhibit a stepwise decrease along the series methane, ethane, compounds containing secondary hydrogen atoms, and compounds containing tertiary hydrogen atoms, which demonstrates that the activation energy is dependent on the nature of the hydrogen atom which is abstracted.^{3,4}

In view of this discrepancy we have studied the reaction between C₃F7 radicals and a compound, here cyclohexane, containing secondary hydrogen atoms. The rates of abstraction from cyclohexane, where there is little strain in the ring, will be almost exactly the same as that for a secondary hydrogen •in a paraffin.

Perfluoro-*n*-propyl ketone was used as a photolytic source of C_3F_7 radicals. Its preparation and purification, the apparatus and procedure were identical to that described previously⁵ except that the reaction cell was 174 ml. The cyclohexane was

(1) This work was supported by a grant from the National Science Foundation.

(2) G. Giacometti and E. W. R. Steacie, Can. J. Chem., 36, 1493 (1958).

(3) E. W. R. Steacie, J. Chem. Soc., 3986 (1956).

(4) G. O. Pritchard, H. O. Pritchard, H. I. Schiff and A. F. Trotman-Dickenson, Trans. Faraday Soc., 52, 849 (1950).

(5) G. H. Miller and E. W. R. Steacie, J. Am. Chem. Soc., 80, 6486 (1958).

Phillips research grade, and was purified and outgassed before use. CO and C_3F_7H were the only products which were collected and measured. Mass spectrographic analysis showed that there was no carry over of any other products or reactants in the respective samples at the temperatures at which they were collected. It is not possible to separate and measure the C₆F₁₄ under the conditions of our experiment.⁶

The results of the experiments are summarized in Table I.

The reaction mechanism for the temperature range 25 to 290° is assumed to be

$C_3H_7COC_3H_7 + h\nu \longrightarrow 2C_3H_7 + CO$	
$C_{3}F_{7} + RH \longrightarrow C_{3}F_{7}H + R$	(1)
$C_3F_7 + C_8F_7 \longrightarrow C_6F_{14}$	(2)
$C_3F_7 + R \longrightarrow C_3F_7R$	(3)
$R + R \longrightarrow R_2$	(4)

where RH is cyclohexane and R is cyclohexyl radical.

For steady-state conditions, that is constant light intensity and small percentage decomposition of the ketone (in these experiments less than 3%), $k_1/k_2^{1/2} = \hat{R}_{C_8F_7H}/R^{1/2}_{C_8F_{14}}[RH]$ where the rate of formation of perfluorohexane $R_{C_{1}F_{14}} = R_{CO} - \frac{1}{2}$ $(R_{C_{i}F_{7}H} + R_{C_{i}F_{7}R})$ from radical balance. We were unable to measure the C_3F_7R formed, so it has been assumed that $R_{C_3F_7R} = 0$. The amounts of C_6F_{14} given in Table I have been calculated in this manner. A least squares plot of the data is shown in Fig. 1. The rate expression is $k_1/k_2^{1/2} = 1.2 \times 10^4 \exp \left[-(5.2 \pm 0.1) \times 10^3/RT\right] \text{ (mole/cc.)}^{-1/2}$ sec. $-\frac{1}{2}$

There is good agreement between the pre-exponential factors for the methane and cyclohexane systems, 9.7×10^3 and 1.2×10^4 (mole/cc.)^{1/2} sec. $-\frac{1}{2}$, respectively. Giacometti and Steacie found in their experiments with methane that the quantities of C3F7CH3 formed were too small for accurate analysis and putting $R_{C_{3}F_{7}CH_{2}} = 0$ did not affect the $k_1/k_2^{1/2}$ values by more than 1%.

However, their treatment for ethane is more complex due to radical-radical disproportionation reactions which can occur in higher hydrocarbon radical systems. In addition to reactions 1', 2', 3'and 4' (identical to reactions 1, 2, 3 and 4, except that RH is ethane and R is ethyl radical).

$$C_3F_7 + C_2H_5 \longrightarrow C_2H_4 + C_3F_7H \qquad (5')$$

and

$C_2H_5 + C_2H_5 \longrightarrow C_2H_4 + C_2H_6$ (6')

must be considered. They analyzed for $C_{5}F_{7}H_{5}$ (from reaction 3') and for butane (from 4'), and

(6) G. H. Miller, G. O. Pritchard and E. W. R. Steacie, Z. physik. Chem., 15, 262 (1958).

TABLE I

Temp., °C.	Products (CD III)									
	Cyclohexane, moles/cc. $\times 10^{6}$	Ketone, moles/cc. $\times 10^6$	$\begin{array}{c} { m CO,} \\ { m moles/cc.} \\ imes \ 10^9 \end{array}$	C_8F_7H , moles/cc. $\times 10^9$	$(CO - \frac{1}{2}C_3F_7H)$ or C ₆ F ₁₄ , moles/cc. $\times 10^9$	Time, sec.	$k_1/k_2^{1/2}, ({ m mole/cc.})^{-1/2}, { m sec.}^{-1/2}$			
23.5	1.33	1.92	5.79	3.36	4.11	540	1.69			
77.5	2.77	3.27	39.6	43.1	18.0	360	6.12			
152.5	1.29	2.61	71.2	97.3	22.5	180	37.6			
172.0	1.32	2.77	50.8	72.7	14.4	120	41.9			
208.8	1.74	3.11	46.3	75.1	8.82	120	41.9			
250.0	1.67	3.69	52.0	92.2	5.88	120	65.9			
293.0	0.702	2.47	46.8	70.3	11.7	120	84.6			

knowing that k_6'/k_4' is 0.12, independent of temperature and pressure, correction for the C_3F_7H formed in reaction 5' can be made. The justification for this procedure is demonstrated by the constancy of the ratio $k_5'/k_3' = 0.40$ over the whole temperature range. $R_{C_6F_{14}}$ was obtained from the radical balance $R_{CO} - 1/2(R_{C_8F_7H} + R_{C_8F_7H_5})$.

The methane and ethane systems are unique in that it is possible to separate out easily the products of the type 3 reaction and measure them. In the cyclohexane system, the C_3F_7 -cyclohexyl is lost and masked in the vast excess of unused reactants. To assess the accuracy of our result we must consider first any error introduced by assuming that reaction 3 is negligible, and second the effect of additional C_3F_7H formed in reaction 5, if reactions 5 and 6 are operative in the system

$$C_{3}F_{7} + R \longrightarrow R(-H) + C_{3}F_{7}H$$
(5)

$$R + R \longrightarrow R(-H) + RH$$
(6)

Whether reaction 5 occurs or not, the $R_{C_{4}F_{14}}$ is given by $R_{CO} - \frac{1}{2}(R_{C_{3}F_{7}H} + R_{C_{5}F_{7}R})$. As reaction 1 is temperature dependent, higher temperatures will lead to greater R radical concentrations, and hence, for the competitive removal of $C_{3}F_{7}$ radicals from the system, $R_{C_{3}F_{7}R}$ will gain over $R_{C_{6}F_{14}}$. So the assumption that $R_{C_{3}F_{7}R} = 0$ leads to an increasing error in $R_{C_{6}F_{14}}$ with temperature. Recalculating Giacometti and Steacie's results for the $C_{3}F_{7}$ + ethane system on the basis that $R_{C_{6}F_{7}H_{5}} = 0$ gives an activation energy for reaction 1' of about 8.0 kcal./mole, an error of 1.2 kcal. in their result, which means our result is low if reaction 3 is important.

Not correcting the rate expression for the C_3F_7H contribution from reaction 5 seems to have little effect on the activation energy for reaction 1. A consideration of this correction to the C_3F_7 + ethane system involves a subtraction of $21.5 \pm 0.5\%$ from the total C₃F₇H formed in the reaction. (This is for 6 of the 10 runs reported; the other runs involve subtractions of 14, 19, 19 and 30%.) In a logarithmic plot this shows up as virtually a constant increment, which does not alter the slope of the line, so that the activation energy for reaction 1' is unaltered, whether the correction is made or not. On this basis we can assume that no appreciable error is introduced by equating the $C_3 F_7 H$ total to that formed in reaction 1, due to the similarity in the two systems. From a steady-state treatment it is not obvious why the ratio of C₃F₇H by $(5)/C_{8}F_{7}H$ by (1) should be a constant, unless at very high C_3F_7 radical concentrations (conditions



Fig. 1.—Arrhenius plot for the reaction of C_3F_1 radicals with cyclohexane.

which do not hold in these experiments) we assume that reactions 3 and 5 swamp reactions 4 and 6 for the removal of R radicals. Then the ratio reduces to $k_{\rm b}/(k_3 + k_{\rm b})$.

Hence, any error in our result is reflected almost entirely in the assumption that reaction 3 does not make a significant contribution to the reaction scheme. For C_2H_5 and C_3F_7 radicals $k_5'/k_3' = 0.40$. It is probable that the ratio k_5/k_3 for cyclohexyl and C_3F_7 radicals is the same or even bigger, which implies a reduction in $R_{C_4F_7R}$ and also to the correction to $R_{C_6F_{14}}$. We consider therefore that our result of 5.2 kcal./mole for $C_3F_7 +$ cyclohexane is in error, but at the most is low by about 1.0 kcal., so that we can estimate that in general C_3F_7 radicals abstract a secondary H-atom from a hydrocarbon with an activation energy of about 6 kcal./mole.

Thus it appears that there is a discrepancy in the results for C_3F_7 with CH_4 and C_3F_7 with C_2H_6 , but further work along the lines of these experiments is unjustified until some more precise method of determining $R_{C_6F_{14}}$ is found, other than radical balance.