The Thermal Decomposition of Ethane. A Note on the Paper by H. Sachsse

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BF$_3$ (Anderson, Lassettre, and Yost)[1]

We find $\omega_2(||)=722$; $\omega_3(\perp)$: $B^{11}=1448$, $B^{10}=1501$ cm^{-1}. $\omega_1(||)=886$ is inactive in the infrared, and $\omega_4(\perp)$ was also located in the Raman effect at 440 cm^{-1}. Yost took ω_3 as 1038 cm^{-1}, but the isotopic doubling in the infrared leaves no doubt that it is considerably higher. K for B—F is 0.669 megadynes/cm. The molecule is plane.

NF$_3$

The fundamental frequencies observed are $\omega_1=908$, $\omega_2=505$ (both $||$), and $\omega_3=1004(\perp)$. The other ($\perp$) frequency ω_4 was estimated to be (420) cm^{-1}. The assignments should be taken as provisional in the absence of Raman data. The molecule is a very flat pyramid, the bond angle being 110° or more. The force constant K for N—F is low, the value 0.410 megadynes/cm corresponding to $r_e=1.45$A, instead of 1.34 from Pauling's data.

CF$_4$ (Yost, Lassettre, and Gross)[2]

We have succeeded in placing the active fundamental frequencies ω_3 and ω_4 at 1252 and 630 cm^{-1}, respectively. Eucken and Bertram[3] assigned ω_3 and ω_4 to two bands observed by them at 1350 and 653 cm^{-1}: the first appears to be a combination tone, and the second is too high. The Urey and Bradley force field[4] for tetrahedral molecules fits CF$_4$ and SiF$_4$ very well: K for C—F is 0.399 megadynes/cm.

SiF$_4$[2]

Of the active fundamentals we found $\omega_3=1022$ cm^{-1}. The other ω_4 was estimated by Yost to lie at (431) cm^{-1}. The inactive modes ω_1 and ω_2 were, respectively, found and calculated by Yost to be 800 and (285) cm^{-1}. K for Si—F is about 0.57 megadynes/cm.

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[1] Anderson, Lassettre, Yost, J. Chem. Phys. **4**, 703 (1936).
[2] Yost, Lassettre, Gross, J. Chem. Phys. **4**, 325 (1936).
[3] Eucken and Bertram, Zeits. f. physik. Chemie **B31**, 361 (1936).
[4] Urey and Bradley, Phys. Rev. **38**, 1970 (1932).

The Thermal Decomposition of Ethane. A Note on the Paper by H. Sachsse

The main theme of the paper by Sachsse in the March issue under the above title is that the new value of E_4 (the activation energy of reaction (4) in the Rice-Herzfeld scheme for the decomposition of ethane) determined by us does not make as large a change in the calculated value of [H] as we say it does, our calculations being in error due to a "misunderstanding." Sachsse then recalculates [H] and shows that even with our value of E_4 the calculated values of [H] are still higher than the observed values of Sachsse by a factor of about 70.

Actually the discrepancy lies in the fact that we used the complete Rice-Herzfeld mechanism *and Rice and Herzfeld's methods of calculation* to get [H]. Sachsse, on the other hand, uses Rice and Herzfeld's set of reaction steps, but calculates the results by assuming steric factors, collision numbers, etc., which they did not use. Furthermore he puts $E_6=8$ kcal. Rice and Herzfeld do not explicitly give E_6, but from a combination of Table A and Eq. (22) of their paper it follows that they use $E_6=0$. This is the value which we used in our calculations.

On the Rice-Herzfeld mechanism $[H]=\left(\dfrac{k_1k_3}{2k_4k_6}\right)^{\frac{1}{2}}$. Assuming, as they do, that all bimolecular velocity constants are given by $k=10^9e^{-E/RT}$, and all unimolecular constants by $k=10^{14}e^{-E/RT}$, we obtain:

(a) *With $E_4=6$ kcal. as found by us, and $E_6=0$ as assumed by Rice and Herzfeld.*

$[H]=1.4\times10^{-12}$, i.e., 4 times *less* than the value found by Sachsse experimentally.

(b) *With $E_6=8$ kcal. as assumed by Sachsse but not by Rice and Herzfeld.*

$[H]=17\times10^{-12}$, which is only 3 times the experimental value.

(c) *Assuming $E_6=0$ and that the reaction occurs by a triple collision so that $a_6=0.001$.*

$[H]=46\times10^{-12}$, which is still within one power of 10 of the experimental value.

We were therefore entirely justified in saying that the value of [H] *calculated from the Rice-Herzfeld mechanism* is in almost exact agreement with Sachsse's experimental value. It follows that Sachsse's argument is with Rice and Herzfeld over the validity of their approximations, and not with our calculations. There was no "misunderstanding" on our part.

It should be emphasized that we are in complete agreement with Sachsse on the main point at issue, namely that our determination of E_4 supports the conclusion reached by Sachsse from his experiments that the Rice-Herzfeld mechanism for the decomposition of ethane is untenable. We argued that while the mechanism with the new value of E_4 now gave the approximately correct value for the hydrogen atom concentration, it could no longer be made to give the correct order or activation energy for the over-all decomposition. Sachsse argues that the predicted value of [H] is still incorrect.

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