

Chemical Kinetics of Bromine Following Neutron Capture

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fessor E. Bright Wilson, Jr., who suggested this problem, for many helpful discussions.

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* The detailed derivation of these terms is contained in a Ph.D. thesis submitted by the author to Harvard University in June 1948.

Chemical Kinetics of Bromine Following Neutron Capture*

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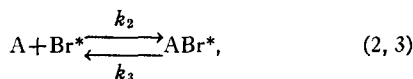
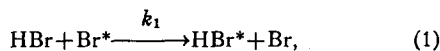
October 13, 1948

THE problem of determining the extent to which a direct correlation exists between photo-chemistry and hot-atom chemistry is one of considerable practical and theoretical interest. Suess¹ initiated a very promising study for the case of $\text{Br}^{79}(\eta, \gamma)\text{Br}^{80}$ by following the distribution of Br^{80} (18 min.) between addition to C_2H_2 and exchange with HBr in the gas phase. Both $\text{C}_2\text{H}_5\text{Br}$ and HBr were used as targets with variable amounts of C_2H_2 . The $\text{C}_2\text{H}_5\text{Br}^*$ and HBr^* were separated by water extraction. Upon the basis of the postulated kinetic Eqs. (1)–(5), and with certain approximations, he showed that the usual steady-state treatment gave

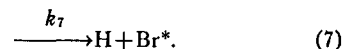
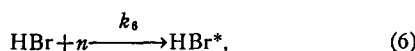
$$\text{organic Br}^*/\text{inorganic Br}^* = a(\text{C}_2\text{H}_2)/b + c(\text{C}_2\text{H}_2),$$

in approximate agreement with his experimental results. He also concluded that there was no evidence of failure to rupture the HBr bond, which he had expected from a consideration of recoil energy and momentum transfer. On the other hand, the $\text{C}-\text{Br}$ bond, with a more favorable mass ratio, would always rupture as a result of the η, γ -process.

Since either qualitative or quantitative interpretation of Suess' results is uncertain because of low precision, unavoidable with a weak neutron source, it seemed desirable to repeat this work with a stronger source. Our experimental procedures approximate his; we have, however, used ethylene instead of acetylene. In addition to Suess' mechanism Eqs. (1)–(5), where A represents either C_2H_2 or C_2H_4 ,



we also formally introduce the η, γ -process, Eqs. (6) and (7), for HBr as target and assume $k_6 = 0$ for $\text{C}_2\text{H}_5\text{Br}$ as target.



This mechanism leads, without approximation, and assuming (Br^*) and (ABr^*) constant, to

$$(A)/(\text{organic Br}^*/\text{inorganic Br}^*) = [(k_1 k_3 / k_2 k_4) + (k_1 (k_4 + k_6) (\text{HBr}) / k_2 k_4)] [1 + (k_6 / k_7)] + [(k_5 / k_4) + (k_6 / k_7) + (k_5 k_6 / k_4 k_7)] (A). \quad (8)$$

The left-hand side (A/R) is expressed in Fig. 1 as a function of ethylene pressure at constant (HBr) ; pressures are expressed in millimeters. Our present experimental results, preliminary in character and somewhat lacking in precision, are consistent with this treatment for Br^{80} (18 min.). It also appears that $k_6/k_7 \approx 0.08$; this ratio probably exceeds zero by more than experimental error.

The non-equality of k_6/k_7 to zero can also be tested by comparing the Br^{80} (18 min.)/ Br^{80} (4.5 hr.) ratios for the water-soluble and water-insoluble activities. Unless the k_6/k_7 ratio happens to be the same for both these η, γ -processes, there should be different activity ratios in the two phases because of chemical discrimination between HBr^* and Br^* . Quite different kinetics for Br^{80} (18 min.) arising from η, γ and isomeric transition could confuse the result, but Suess^{1b} found substantially similar behavior for the two cases. We find, for one-hour neutron bombardment of gaseous HBr with added C_2H_4 and carrier $\text{C}_2\text{H}_5\text{Br}$, that the ratio of activities Br^{80} (18 min.)/ Br^{80} (4.5 hr.) differs between the phases and corresponds, approximately, to $k_6/k_7 = 0$ for Br^{80} (4.5 hr.).

We are preparing to study rather fully, with improved apparatus and better precision, the gas kinetics of nuclear processes involving Br^{80} (18 min.), Br^{80} (4.5 hr.), and Br^{82} to determine what special effects, if any, are associated

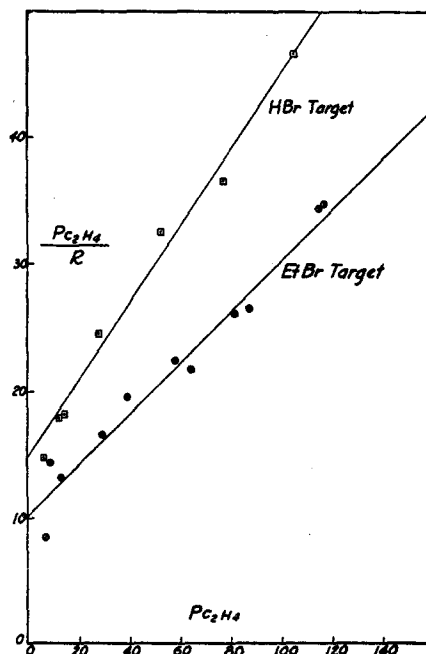


FIG. 1. Test of Eq. (8) for $\text{Br}^{79}(\eta, \gamma)\text{Br}^{80}$ (18 min.).

with high recoil energy from the η , γ -process and with electric charge from the internal conversion which accompanies isomeric transition. We also plan to study eventually the corresponding kinetics for chlorine and iodine.

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Linear Atomic Chain and the Metallic State

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 July 8, 1948

IT is known in the quantum mechanics of molecules that from the molecular orbital method and the valence bond method the former one is more adapted to describe larger molecules, especially if unlocalized bonds are present. The electrons forming such bonds have just the properties that they cannot be fixed on individual atoms or between any two neighboring atoms, but they show their effect practically distributed to the whole molecule. So they show great analogy with the valence electrons of the metals. We now proceed to apply the M.O. method in the LCAO approximation to some problems concerning metals.¹ This method is here adapted to treat a linear arrangement of similar atoms. Even this very simple model shows typically the development of the metallic properties. We restrict ourselves to the treatment of atoms with only one valence electron, arranged at equal distances from one another.

The molecular orbitals can be written $\psi_m = \sum_{i=1}^n c_{mi} \varphi_i$, where $\varphi_1, \varphi_2, \dots, \varphi_n$ are the normalized eigenfunctions of the valence electrons of each of the n atoms constituting the chain. The φ_i 's are here identical eigenfunctions, i denoting the nucleus to which they are related. The coefficients c_{mi} and the energy E_m can be determined by the usual degenerate first-order perturbation method. Taking the simplified assumption that only neighboring atomic orbitals interact, the other interactions being negligible, we form the integral $\beta = \int \varphi_i^* H \varphi_{i+1} dv$, where H is the Hamiltonian of the whole system, which can be replaced, in the approximation used, by the Hamiltonian of the diatomic molecule consisting of the atoms i and $i+1$. Similarly, we neglect overlap integrals except those of two neighboring orbitals, i.e., $S = \int \varphi_i^* \varphi_{i+1} dv$. The integrations are to be extended to the whole space. The secular equation of this problem will be now

$$\begin{vmatrix} W & \beta' & 0 & \cdots & 0 & 0 & 0 \\ \beta' & W & \beta' & \cdots & 0 & 0 & 0 \\ 0 & \beta' & W & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & W & \beta' & 0 \\ 0 & 0 & 0 & \cdots & \beta' & W & \beta' \\ 0 & 0 & 0 & \cdots & 0 & \beta' & W \end{vmatrix} = 0. \quad (1)$$

Here is $W = Q - E$, where $Q = \int \varphi_i^* H \varphi_i dv$ is the Coulombic energy of the electron in the valence orbital of the i th atom; E denotes the required energy of the molecular orbital—further, we have used $\beta' = \beta - ES$. The eigenvalues E can be determined from Eq. (1), which is of grade n in E . One can easily see that the solutions of (1) are

$$E_m = Q - 2\beta \cos(\pi m/n + 1)/1 - 2S \cos(\pi m/n + 1), \quad (m = 1, 2, \dots, n). \quad (2)$$

The possible energy terms are consequently in an energy band, the bottom of which we get by taking $m = n$, and the top of which by taking $m = 1$, since Q and β are negative; further, we have $QS > \beta$ practically always.

The orbitals belonging to these terms must be populated by the n electrons available according to the Pauli principle; i.e., at absolute zero temperature each of the $n/2$ deepest terms of (2) must be occupied by two electrons if n is even, or each of the $n-1/2$ deepest terms of (2) by two electrons and the next higher term by one electron if n is odd. If $n \rightarrow \infty$, the two cases yield the same limit, so we can restrict ourselves to the case of even n . The eigenvalues of (2) belonging to the $n/2$ lowest states are those with $m = n, n-1, \dots, n/2+1$.

One can show, generally, that the average energy of the electrons lies lower than that of the electron in the atom, moreover, lower than that of the electrons in the diatomic molecule. The calculation will be extremely simple if we neglect S . In this case we get the average electronic energy

$$\begin{aligned} \bar{E} &= (2/n) \sum_{m=(n/2)+1}^n E_m \\ &= Q - (4\beta/n) \sum_{m=(n/2)+1}^n \cos(\pi m/n + 1) \\ &= Q - (2\beta/n) + (2\beta/n \sin(\pi/2(n+1))). \quad (3) \end{aligned}$$

One can show that Eq. (3) decreases steadily with n , so that any new atom which lengthens the chain makes the average energy deeper. In the case of $n \rightarrow \infty$ we get

$$\bar{E} = Q + (4/\pi)\beta = Q + 1.27\beta, \quad (4)$$

which shows that our infinite chain is stable against dissociation into atoms by 1.27β and against dissociation into molecules by 0.27β . If we do not neglect S , we have for $n \rightarrow \infty$, if $|S| < \frac{1}{2}$,

$$\bar{E} = (\beta/S) + (2(QS - \beta)/\pi S(1 - 4S^2)^{1/2}) \arccos(-2S). \quad (5)$$

The next step is the determination of Q , β , and S . If we treat atoms for which we know the valence orbitals, we can calculate these quantities as functions of the lattice constant and minimize (5) with respect to this parameter. So we can calculate the values of the lattice constant, the total energy, the sublimation energy, and the band width by the formulas given above. So, for instance, we get by this rough calculation with Li eigenfunctions given by Duncanson and Coulson² for the lattice constant 3.7Å, for the total energy per electron 6.23 eV, for the sublimation energy 0.64 eV, and for the width of the energy band at this lattice distance 8.19 eV. These results should not be seriously compared to the experimental results of a real metal—first of all because the latter has a space configura-