chloride and nitrogen dichloride; that the dichloride combines with nitric oxide to form dichlorodinitrogen oxide; that this compound decomposes very rapidly at $-80°$ but that it is sufficiently stable at $-150°$ to yield a second chlorine atom to nitric oxide before it decomposes; and that this reaction is much more rapid than the combination of nitric oxide and chlorine at that temperature.

3.   The rather rapid combination of nitric oxide with chlorine at $-80°$ explains the excess of nitric oxide used and the excess of nitrosyl chloride found as compared with those required by the equation given.   It also explains the deficiency of chlorine.   The excess of nitric oxide and nitrosyl chloride and deficiency of chlorine at $-150°$ may be explained in the same way or by supposing a further reaction of nitric oxide with a hypothetical monochlorodinitrogen oxide.

4.   No satisfactory evidence was obtained that nitrogen dioxide is formed in the reactions studied.

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THE POSSIBILITY OF BIMOLECULAR ASSOCIATION REACTIONS

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It seems to have been first pointed out by Herzfeld[1] that the recombination of atoms to form a diatomic molecule could not be a bimolecular process, but must occur either on the walls or at triple collisions; Herzfeld calculated the mean life of the molecules which could result from simple collisions and obtained values of the order of 10^{-12} sec.; such a time is scarcely greater than the rather indefinite duration of a collision, which has, of course, exact meaning only after an arbitrary definition has been given.   The details of this calculation might be changed slightly if it were to be repeated in the light of more recent knowledge, but the result would surely be unchanged.   Furthermore, there is a considerable body of experimental material, all of which shows that diatomic molecules are not ordinarily formed at binary collisions.

There has been some tendency to generalize this statement and say that no bimolecular association reaction is possible, or at least that it will occur with only a negligible rate.[2]   Now it is certainly true that bimolecular association reactions can occur, because this process is the reverse of unimolecular decomposition, and there are known some dozen reactions which are of this type, beyond any reasonable doubt.   Such an argument

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[1] Herzfeld, *Z. Physik*, **8**, 132 (1922).

[2] This view has been frequently expressed by H. S. Taylor and recently by Taylor and Eméleus, THIS JOURNAL, **53**, 562 (1931).   It has been held by numerous other workers also.

has been, and still remains, of a rather academic character, because of the known unimolecular reactions not one leads to a measurable equilibrium at the temperatures of the rate measurements; it is true that the disso· ciation of nitrogen tetroxide is very probably a unimolecular reaction, but this hypothesis does not have a shred of experimental evidence to support it. The study of polymerization processes in hydrocarbon vapors which has been made at Princeton during the last few years is making association reactions accessible to reaction-rate studies; fairly recently Pease[3] has presented rather definite evidence that under suitable circumstances the polymerization of ethylene is a second order reaction. The question whether such a reaction can have a true bimolecular mechanism thus becomes of real interest. It will be shown in the present paper that such a mechanism is perfectly possible, at least on general theoretical grounds.

From a practical consideration the reason why a diatomic molecule cannot be formed at a binary collision is that the energy of the reaction, which is necessarily greater than the heat of dissociation, cannot be removed from the molecule's only bond. For although it may possibly be emitted as radiation, or stored either as electronic or as rotational energy, detailed analysis shows that the probability of any of these occurrences is very small; hence, except at a minute fraction of all collisions, the molecule formed must dissociate immediately. That is to say, if a diatomic molecule has enough energy to dissociate, it will do so at once; there is, in the reverse case, no time lag between activation and reaction. Since it is upon the existence of such a time lag that the possibility of unimolecular reaction rests, we know experimentally that for more complex molecules there is such a time lag. The order of magnitude of this lag can be computed from experimental data without reference to any detailed theory of unimolecular reaction, because in any case it must be, on the average, not much different from the mean free time at pressures such that the reaction is just beginning to deviate from a first order course. In most cases, the time lags found in this way are of the order of 10^{-9} to 10^{-7} sec. A complex molecule, once formed at a binary collision, may then be stabilized at any subsequent collision within this period; the stabilizing molecule may thus have been, in some cases, as much as 0.01 cm. distant at the instant of formation of the complex; such a process can hardly be considered a triple collision.

We must next consider the second objection to such a process; this is that in the large majority of binary collisions no complex can be formed because of quantum restrictions. This objection also seems to disappear upon analysis. The restrictions which have to be considered are the conservation of energy, of momentum and of angular momentum, to-

[3] Pease, THIS JOURNAL, **52**, 1158 (1930); **53**, 613 (1931).

gether with the quantization of rotation and of vibration. It has already been shown by Beutler and Rabinowitsch[4] that the quantum mechanical uncertainty principle completely destroys the restriction based on the conservation of angular momentum and the quantization of rotation. This principle will at the same time relax somewhat the restriction arising from conservation of momentum, though it is not clear just how this is to be treated. There remains to be considered the possibility of satisfying at once the conservation of energy and the vibrational quantum conditions. Now it must be remembered that the quantum states in which we are interested are not real stationary states, because they have finite mean lives; this has the important result that they do not possess sharply defined energy; the relation between the mean life and the vagueness in the energy is given by the well-known equation

$$\tau = h/\Delta E \tag{1}$$

There will thus be a finite chance that the energy available for the vibrational degrees of freedom will lie within some quantum state. It is important to try to form some estimate of the actual magnitude of this chance, and to do this we need to know how closely the vibrational states are spaced. Consider a molecule with s vibrational degrees of freedom and a total of n quanta of energy distributed among them. If all of the associated frequencies are different, then each distribution will have a different total energy; it is well known that the number of such distributions is

$$\frac{(n + s - 1)!}{n! \, (s - 1)!} \tag{2}$$

Now, since the various frequencies are all different, there will not be any simple relation between the total energy of a distribution and the number of quanta which it involves; that is, there will be pairs of states such that the one with more quanta has less energy. Nevertheless, it seems that no great error will be made in taking the total number of distributions whose energy is between that of n and $n + 1$ mean quanta as given by (2). Numerical tests in several cases, for moderate values of n and s, always gave divergences in the direction of slightly greater numbers than predicted by (2). By using (2) in connection with an estimated (or assumed) mean quantum for the molecule concerned, we are able to calculate the average spacing between energy levels; this may be combined with the average width of energy levels to give the fraction of energy values within a given range which correspond to a quantum state. We shall proceed to make such calculations.

The most satisfactory energy unit for these purposes is the reciprocal second—that is, the energy of the quantum with unit frequency; this value is equal to 6.55×10^{-27} ergs, or about 10^{-10} cal./mole. Suppose

[4] Beutler and Rabinowitsch, Z. physik. Chem., **8B**, 231 (1930).

that the heat of reaction plus the heat of activation is 10^{15} sec.$^{-1}$, or about 100,000 cal./mole. If we take the rather large value of 10^{14} sec.$^{-1}$ for the mean energy of a vibrational quantum, we will then have $n = 10$; the value will in most cases be rather larger than this, but we purposely begin with an unfavorable case. The value to be used for s is $3(m - 2)$, where m is the number of atoms in the molecule being formed; to allow for the fact that all of the vibrational states may not have different frequencies, we take a somewhat smaller value; thus a molecule with 10 atoms might have $s = 24$; we shall make the calculations for $s = 6, 8$ and 10. Taking $s = 6$, we see by (2) that the number of different energy levels with 10 quanta will be $15!/5! \times 10! = 3003$; these states are within an energy range of 10^{14} sec.$^{-1}$, so that the mean distance between adjacent states is 3×10^{10} sec.$^{-1}$; this is rather larger than the width of a level, and under such circumstances only a small fraction of all collisions could result in reaction. With $s = 8$, however, we find a mean spacing of 5×10^9 sec.$^{-1}$, and with $s = 10$ we get 10^9 sec.$^{-1}$. If we use instead of $n = 10$ the more likely value $n = 15$, and keep $s = 10$, we find for the mean spacing a value 8×10^7 sec.$^{-1}$. If we push the values of n and s anywhere near the upper limits of plausibility, we obtain values for the mean distance between levels much less than the mean width of a level as determined from the time lag. It is thus possible that in some cases any energy value will correspond to some quantum state, while in other cases the chance for such a correspondence may be 0.1, 0.01 or even less. As a general rule, we should expect that the chance for correspondence would increase with the complexity of the molecule being formed, though the influence of specific factors will probably be a great one. This calculation tells us nothing, of course, about the efficiency with which reaction will occur even when all the energy and quantum conditions are satisfied.

We may consider in a little more detail the application of these ideas to Pease's work on ethylene polymerization. This reaction is second order between 2.5 and 10 atm.; at 1 atm. there is some evidence for a rate less than that predicted by the second order equation. The energy of activation determined from the temperature coefficient is given by Pease as 35,000 cal.; when this value is used in the simple expression $Ze^{-E/RT}$ to calculate the reaction rate, a value is found about 2000 times that observed. Pease interprets this as meaning that only in $1/_{2000}$ of the collisions can the energy and quantum conditions be satisfied. He gives also an interpretation suggested by Taylor; this is that every collision which supplies the necessary reaction energy leads to formation of an unstable complex which either dissociates spontaneously, or survives until it colloids with a molecule of ethylene, whereupon it may be stabilized or may be destroyed; if the odds in favor of destruction are 2000:1, this mechanism gives a reaction which will be second order at high pressure,

but will deviate when the pressure is low enough, and will give the correct absolute rate. The interpretation which the present writer would suggest is of an intermediate nature. There does not seem to be sufficient evidence to decide how the low efficiency is apportioned between a low yield for the formation of the dissociable complex and a low yield for the stabilization process; if the formation of the complex has a low yield, however, this need not necessarily be blamed on the necessity of satisfying a quantum condition, as Pease has suggested; in the decomposition of nitrogen dioxide, a bimolecular reaction which is not an association, the rate is only about $1/_{200}$ of that calculated in the usual way from the activation energy and recent work by Hartel and Polanyi[5] furnishes other examples of low efficiencies. We thus suppose that collisions which are able to supply the necessary activation energy result, with an unknown efficiency, in formation of a complex which is capable of spontaneous dissociation; this complex may, however, be stabilized by collision with a molecule of ethylene; here again the process may not be 100% efficient; the product of the two efficiencies is about $1/_{2000}$. The experiments do not supply any evidence in favor of a specific effect of ethylene in stabilization; it is quite probable, however, that ethylene and the reaction product, butene, are more efficient than inert gases, because in almost all unimolecular reactions it has been found that the reacting substance and its decomposition products are more effective in maintaining the rate than are indifferent gases; this means, of course, that the efficiency of energy transfer at collision is greater. If the second order reaction rate falls off at a pressure as high as one atmosphere in this case, then the mean time lag between formation of a complex and its dissociation is about 3×10^{-10} sec., and the mean width of a quantum state 3×10^{9} sec.$^{-1}$. With a value this large, it should be easy for the energy and quantum conditions to be satisfied. The distance of the stabilizing molecule at the instant of formation of the complex would then be rather smaller than usual, about 10^{-5} cm. Even in this case, however, it would seem an exaggeration to speak of the event as a triple collision.

Summary

Calculations have been presented to show that the formation of complex molecules by a bimolecular association process should be possible at a considerable fraction of all collisions so far as the conservation laws and the quantum conditions are concerned. The polymerization of ethylene appears to be an example of such a reaction.

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[5] Hartel and Polanyi, *Z. physik. Chem.*, **11B**, 97 (1930).