THE QUENCHING OF MERCURY RESONANCE RADIATION. II. FURTHER HYDROCARBONS AND NITRIC OXIDE[1]

BY JOHN R. BATES

The effectiveness of the hydrocarbons of the series methane, ethane, propane and butane in quenching the resonance radiation of mercury was given in Part I. The work here presented[2] extends these measurements to hydrocarbons containing a larger number of carbon atoms representing the saturated, unsaturated and benzene hydrocarbons. Nitric oxide is included as one of the few diatomic gases which have not been measured by the improved method used,[3] although Noyes[4] has published an estimated effective cross section obtained in his investigation of the decomposition of this gas under the influence of excited mercury atoms. It was hoped that an extension to as large a number of molecules as possible would aid in a clarification of the theories connected with the structure of molecules and their ability to take over the energy of excitation of mercury atoms in the 2^3P_1 state.

Experimental

The methods of measurement are given in Part I of this work. In measuring low pressures of the high-boiling hydrocarbons it became necessary to use the gage described by Foote and Dixon[5] for the measurement of liquids of low vapor pressures. An additional refinement, which removed the necessity of constantly checking the temperature of the liquid mercury supplying mercury vapor to the resonance lamp and quenching vessel, was added. Water from a thermostat constant to within 0.1° was pumped through the Dewar flasks in which these mercury reservoirs were placed.

In working with the non-volatile hydrocarbons it was found that no stopcocks could be used in the system, since the vapors of these substances dissolved in the stopcock grease and then, upon pumping, evaporated slowly, or even evaporated from the grease on the other outlet of the stopcock, making the regulation and measurement of pressures impossible. All stopcocks were, therefore, replaced by mercury cut-offs.

The pure hydrocarbons were dried over phosphorus pentoxide and subjected to fractional distillation *in vacuo*. The nitric oxide was prepared by the action of a solution of sodium nitrite in concentrated sulfuric acid upon liquid mercury. The gas was then dried with phosphorus pentoxide,

---

[1] Presented at the Fall Meeting of the American Chemical Society, Buffalo, 1931.

[2] Bates, THIS JOURNAL, **52**, 3825 (1930).

[3] Zemansky, *Phys. Rev.*, **36**, 919 (1930).

[4] Noyes, THIS JOURNAL, **53**, 514 (1931).

[5] Foote and Dixon, *ibid.*, **52**, 2170 (1930).

and subjected to a vacuum distillation. It was stored in a bulb containing mercury droplets, which remained untarnished after several months, showing the absence of oxygen in the gas. Had oxygen been present the nitrogen peroxide resulting from its reaction with nitric oxide would have rapidly tarnished the mercury surfaces.

Experimental Results

The values of J, the percentage of resonance radiation emitted, are given below for various pressures of the gases. The pressures are expressed in millimeters of mercury.

TABLE I
EXPERIMENTAL VALUES

n-Heptane		2,2,3-Trimethylbutane		Benzene	
P, mm.	J	P, mm.	J	P, mm.	J
0.0220	90.0	0.0487	85.8	0.008	92.3
.0308	86.5	.096	71.9	.013	87.6
.0432	82.6	.136	64.6	.024	82.2
.0489	81.9	.154	60.2	.039	75.5
.0510	82.0			.078	64.1
.0690	74.9				
.0899	69.0				
.0930	69.0				
.119	62.8				
.124	61.0				

Nitric oxide		1 Heptene		3 Heptene	
0.0207	87.1	0.0123	90.4	0.0162	83.3
.0264	83.4	.022	84.9	.0287	75.3
.0331	76.9	.022	81.9	.0527	65.3
.0507	71.5	.022	81.4	.084	55.9
.108	50.7	.029	76.4	.171	38.5
		.053	67.9		

From these values of P and J may be obtained the value of GK/P, where K is the number of effective collisions per second and $G = 10^{-7}$ the mean life of the excited mercury atom, and Σ_E^2, the effective cross section of the collision process, Σ_E being the sum of the effective radii in collision. The method of calculation appears in the earlier work. These values are tabulated in Table II.

TABLE II
CALCULATED VALUES

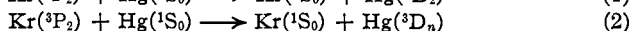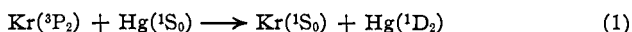|	GK	$\Sigma_E^2 \times 10^{16}$		GK	$\Sigma_E^2 \times 10^1$
Nitric oxide	1.25	24.7	3-Heptene	1.78	55.9
n-Heptane	0.760	24.0	1-Heptene	1.46	45.8
2,2,3-Trimethylbutane	0.625	19.7	Benzene	1.42	41.9

Discussion of Results

The values of the effective cross sections of these molecules are without exception the largest that have been found, with the use of the method here

employed, which, according to the theoretical calculations of Zemansky,[6] gives a more accurate value than those previously in use.   However, for the larger molecules it is not surprising that this should be the case.

In considering the relation of effective cross section to the structure of the molecule, there are several factors which must be taken into account. These may be divided, in a purely formal manner, into three classes, electronic, energetic and spatial.

The principle of conservation of spin angular momentum of the electronic system of two atoms in collision was proposed by Wigner,[7] and Beutler and Eisenschimmel[8] have tested it experimentally and found that in energy transfers where it is obeyed there is a much greater probability than in those cases where there is a change in total spin angular momentum in the energy interchange.   Thus collisions in which a krypton atom in a triplet (2^3P_2) state gives its energy of activation to a mercury atom (1^1S_0) raising it to a singlet state (5^1D_2) are much less probable than those which result in a mercury atom in a triplet (5^3D_n) state, since the krypton atom falls to a singlet state (1^1S_0) and the total spin or multiplicity remains the same in the latter case.   Thus in the two equations

$$Kr(^3P_2) + Hg(^1S_0) \longrightarrow Kr(^1S_0) + Hg(^1D_2) \qquad (1)$$
$$Kr(^3P_2) + Hg(^1S_0) \longrightarrow Kr(^1S_0) + Hg(^3D_n) \qquad (2)$$

the total spin on the left-hand side is equal to 1 in both cases, while on the right (1) gives a spin of 0 and (2) a spin of 1, the same as the original two molecules.

It must be pointed out that the principle is identical with the spectroscopic selection rule which states that only terms of like multiplicity can intercombine, which in helium is obeyed, but in large atoms such as mercury breaks down, since, for example, the strong 2536 line of mercury is a $^3P_1 \longrightarrow {}^1S_0$ transition.   It does not, therefore, hold that the "forbidden" transfers of energy will be completely absent, but that they will be considerably less frequent.   It might also be mentioned that the rule will hold for the steps in chain reactions.

Of the molecules which have been measured all are in a singlet state with the exception of oxygen, which has a $^3\Sigma$ normal state and nitric oxide which has a $^2\Pi$.

Hydrogen has already been treated by Beutler and Eisenschimmel who showed that either of the two dissociation processes

$$H_2(^1\Sigma) + Hg(^3P) \longrightarrow H(^2S) + H(^2S) + Hg(^1S)$$
$$H_2(^1\Sigma) + Hg(^3P) \longrightarrow H(^2S) + HgH(^2\Pi) + Hg(^1S)$$
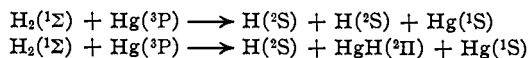
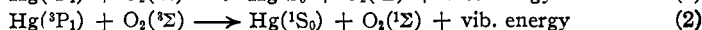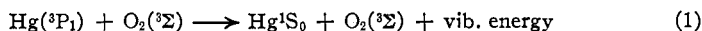is in accord with the conservation of spin, and also energetically possible.

[6] Zemansky, *Phys. Rev.*, **36**, 919 (1930).

[7] Wigner, *Nachr. Götting. Ges.*, 375 (1927).

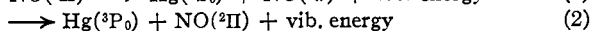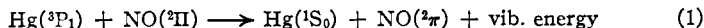[8] Beutler and Eisenschimmel, *Z. physik. Chem.*, **10**, 89 (1930).

Leaving out of consideration for the present these three cases, we find that the effective cross sections of the remaining molecules are considerably less than the normal cross sections as determined from gas kinetic data. Furthermore, there exists evidence that the molecules N_2, CO, NH_3, CH_4 and H_2O quench the $^3P_1$ mercury atom to the $^3P_0$ metastable level, while there is no indication one way or the other for CO_2, C_2H_6, C_3H_8, C_4H_{10}, although Zemansky assumes these to do the same thing. If the mercury atom should lose its energy to return to the ^1S normal state and the molecule receiving the energy remains in its normal $^1\Sigma$ state, but in a higher vibrational state, the spin angular momentum would not be conserved. However, in the drop of the mercury from $^3P_1$ to $^3P_0$ with the quenching molecule remaining a $^1\Sigma$ the total spin remains unchanged, and we see this to be the preferred process, at least for the cases mentioned. It should perhaps be emphasized that the evidence for this transition, which consists in observing absorption of mercury of lines which originate in the $^3P_0$ state[9] and also the apparent decrease in quenching at high pressures or temperatures,[10,2] does not at all preclude the possibility that some fraction of the mercury atoms are being quenched to the normal state. It does, however, show that the transition $^3P_1 \longrightarrow {}^3P_0$ is very prevalent, which it should be if the conservation of spin represents a large factor in the probability of transition.

In the case of O_2 and NO we find cross sections larger than those obtained from gas kinetic data. There are two possible ways in which the oxygen molecule can take up the 4.86 volts of energy which are given up in the $^3P_1 \longrightarrow {}^1S_0$ transition

$$Hg(^3P_1) + O_2(^3\Sigma) \longrightarrow Hg^1S_0 + O_2(^3\Sigma) + \text{vib. energy} \qquad (1)$$
$$Hg(^3P_1) + O_2(^3\Sigma) \longrightarrow Hg(^1S_0) + O_2(^1\Sigma) + \text{vib. energy} \qquad (2)$$

It is obvious that both (1) and (2) have the spin conserved. Wigner (private communication) considers that (2) would, on the basis of spin, be more probable by a factor of three than would (1).

With NO either of these two processes answers the spin requirements

$$Hg(^3P_1) + NO(^2\Pi) \longrightarrow Hg(^1S_0) + NO(^2\pi) + \text{vib. energy} \qquad (1)$$
$$\longrightarrow Hg(^3P_0) + NO(^2\Pi) + \text{vib. energy} \qquad (2)$$

From the consideration of the ability of the molecules to receive the energy of the mercury atom it has been shown theoretically by Kallman and London[11] and Rice[12] that the closer the energy level of the receiving atom or molecule to the energy to be received, the more probable the transition. Beutler and Josephy[13] have studied the transition between

[9] R. W. Wood, *Proc. Roy. Soc.* (London), **106**, 679 (1924); *Phil. Mag.*, **50**, 774 (1925); Wood and Gaviola, *ibid.*, **5**, 271 (1928).

[10] Cario and Franck, *Z. Physik*, **17**, 202 (1923).

[11] Kallman and London, *Z. physik. Chem.*, [B] **2**, 207 (1929).

[12] Rice, *Proc. Nat. Acad. Sci.*, **17**, 34 (1931).

[13] Beutler and Josephy, *Z. Physik*, **53**, 747 (1929).

excited mercury atoms and sodium atoms and indicated that this can be shown experimentally. Zemansky has classed the cross sections obtained for transitions from $^3P_1$ to $^3P_1$, which represents an energy of 0.218 volt and again shown that the closer an energy state of the molecule is to this value the larger the cross section. However, in choosing between the two possible jumps $^3P_1 \longrightarrow {}^3P_0$ and $^3P_1 \longrightarrow {}^1S_0$ it is not possible to use the energy resonance as a criterion. For example, N_2 and CO have vibration levels which lie at 4.86 and 4.82 volts, as determined by extrapolating the expressions for their vibrational frequencies given in the "International Critical Tables." These are in much closer agreement to 4.86 volts than are the first vibrational levels to 0.218 volt, which is the energy difference between the $^3P_1$ and $^3P_0$ states.

Thus the energy relationships hold true only in the cases of a single type of electronic transition which, as has been shown, may quite conceivably be governed by the necessity of having the total spin conserved. In the cases of O_2 and NO where this latter selection rule is obeyed and it seems possible to have the whole 4.86 volts transferred, there are also vibrational energy levels in these molecules fairly close to this value; namely, 4.86 for $O_2{}^3\Sigma$, 4.90 for $O_2{}^1\Sigma$ and 4.90 for $NO^2\Pi$.[14] Zemansky suggests that the mercury atom reacts with the oxygen molecule $Hg' + O_2 \longrightarrow HgO + O$ but as Noyes points out an error crept into his calculations and the close energy agreement to which he ascribes the large cross section for oxygen is non-existent. The process is also doubtful because of chemical evidence which shows that more oxygen molecules are activated than there are mercury atoms present in the system.

For diatomic molecules there is no necessity for a consideration of the space occupied by the two atoms since this is introduced in the eigenfunctions whereby the probabilities are calculated. Moreover, the differences in the cross section due to this would be negligible in comparison with the other factors. However, as we go up an homologous series of compounds such as the saturated hydrocarbons it is obvious that the effective cross section must depend to a progressively larger extent on the space configuration of the atoms of the molecule. Not only is it a matter of placing the carbon atoms in an alternating chain which is demanded by the tetrahedral nature of the valence forces of the carbon atom, but also, due to the fact that there exists free rotation around a single carbon–carbon bond, there are more and more possible arrangements for the configuration as the number of carbon atoms increases above three. This effect increases the effective area offered to a colliding atom by such molecules. Zemansky, in incorporating into his results the values for the cross section of the hydrocarbons, does not take this into consideration, though it would probably be of some importance in the case of butane. The value of the

[14] A. C. G. Mitchell, *J. Franklin Inst.*, **206**, 817 (1928).

cross section for heptane, furthermore, does not fit into Zemansky's curve for the variation of this magnitude with the difference in energy between the nearest infra-red band of the molecule and the 0.218 volt which the mercury atom gives up. The band in heptane, according to the data of Coblentz,[15] from which the data of Zemansky were also derived, should be at 5.81, which is equivalent to 0.212 volt.[16] This value should, according to his curve, give a cross section smaller than butane, while actually it is almost five times as large. This is almost certainly due to these spatial considerations. In discussing these hydrocarbons, it must also be borne in mind that there exists no evidence that the quenching is to the meta-stable level, except in the case of methane. In fact the work of Taylor and Hill,[17] who showed that the hydrocarbons, with the exception of methane, are decomposed by excited mercury atoms, lends considerable doubt to the supposition that these molecules quench by the deactivation process $2^3P_1 \longrightarrow 2^3P_0$. While the decomposition might occur by a double deactivation process $2^3P_1 \longrightarrow 2^3P_0 \longrightarrow 1^1S_0$, the second step furnishing the energy necessary to break up the molecule, there are no grounds upon which to base the assumption of such a complicated mechanism. For these reasons it would seem that the hydrocarbons, with the exception of methane, should not be taken into account in considering the variation of effective cross section with the resonance between the energy states of molecules and the energy difference between the 2^3P_0 and 2^3P_1 levels of mercury.

The value of Σ_E^2 for nitric oxide of 24.7×10^{-16} sq. cm. is the largest cross section found among the diatomic molecules. The value obtained by the method employed here is very much larger than the value of 2.10×10^{-16} reported by Noyes in his measurements. However, Noyes in a private communication has informed the author that a recalculation of his results has raised his cross section to a value not incompatible with the result here presented, when the differences in experimental method are considered. As has been discussed in an earlier section, the principle of conservation of spin angular momentum is obeyed for both processes of deactivation of mercury by nitric oxide. Noyes has discussed at length the various possible mechanisms whereby the nitric oxide might act with mercury. He has come to the conclusion that his work gives some evidence that the process involves the $2^3P_1 \longrightarrow 2^3P_0$ transition of the mercury atom. If, now, we plot the values of Σ_E^2 against the energy values of the vibrational frequencies expressed in volts of the molecules involved, we obtain the results shown in Fig. 1. The point 0.218 volt represents the

[15] Coblentz, "Investigations of Infra-Red Spectra," Carnegie Institute of Washington, 1905.

[16] *n*-Heptane is not measured by Coblentz, but both *n*-hexane and *n*-octane have this band at this wave length, from which there is apparently no large deviation even up to hydrocarbons of very long chain length $(C_{24}H_{50})$.

[17] Taylor and Hill, This Journal, **51**, 2922 (1929).

energy of $2^3P_1 \longrightarrow 2^3P_0$ transition of the mercury atom. The line at 0.244 represents the addition to this of the average kinetic energy, kt, possessed by the colliding atoms and molecules. The curve thus obtained is symmetrical to either of these two points. The values of the hydrocarbons are omitted and the value for carbon dioxide should perhaps not be used in this connection since it is not at all established that this molecule brings about the transition here under consideration. It is merely plotted to show how far off any resonance curve it falls. Zemansky, due to his inclusion of the hydrocarbons, was led to believe that it was carbon monoxide which did not agree with the other values. The latter molecule is however known to produce transitions to the metastable level, and fits the curve very well if the hydrocarbons are not included and the value for nitric oxide is taken into consideration. It is not to be expected that these points will lie on a smooth curve, as there are variables other than the energy resonance which must be taken into consideration. For example, the masses of the molecules will alter the probability of energy transfers in collisions of the second kind.[18] This type of curve is, however, in agreement with the results derived theoretically, even to the asymmetry of the resonance curve.[19]
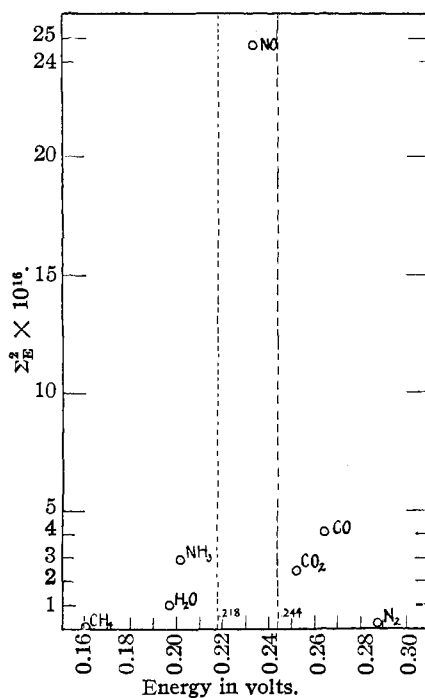

Fig. 1.

The large cross section for the two heptenes is undoubtedly connected with the presence of the double bond. As to the existence of such a large difference in the cross sections of the two isomers, this may be due to the effect on spatial arrangement of the molecule of the fact that there is no rotation around a double bond.

[18] Morse and Stueckelberg, *Ann. Physik*, [5] 9, 579 (1931).

[19] The statement of Morse and Stueckelberg that the asymmetry of the resonance curve found by them theoretically is borne out by Zemansky's experimental values is incorrect. The position of the asymmetry found by the latter is directly opposite to that predicted. This, however, is not surprising, since the cross section will be affected by factors other than the energy difference, which is not allowed for in either curve. In fact, it is a mistake to draw a curve through the experimental curves without correcting for the other factors involved.

The size of Σ_E^2 for benzene, which is greater than the gas kinetic value of 21.9, is of interest principally because in the work of Bates and Taylor[20] this substance, when subjected to the action of excited mercury atoms, gave very little permanent gas. As was observed in that work the action of the mercury probably results for the most part in the removal of a hydrogen atom, which then recombines with other benzene molecules to form hydrobenzenes.

The author is indebted to the Research Laboratories of the General Motors Corporation for the pure hydrocarbons used in these measurements.

Summary

The quenching of mercury resonance radiation by nitric oxide, benzene, n-heptane, 2,2,3-trimethylbutane, 2-heptene and 3-heptene has been measured, and values of the effective cross sections of these molecules have been calculated. A general arrangement of molecules which correlates their effective cross sections and structure has been discussed.

[20] Bates and Taylor, THIS JOURNAL, 49, 2483 (1927).

PRINCETON, NEW JERSEY

SOLUBILITY OF THALLOUS CHLORIDE IN SOLUTIONS OF GLYCINE AND GLYCINE SALTS[1]

BY CRAWFORD F. FAILEY

The solubilities of salts in the presence of amino acids have been little investigated. Bjerrum[2] reported the solubility of dinitrotetramminecobaltinitrate $[Co(NH_3)_4(NO_2)_2]NO_3$ as about 8% greater in $N/10$ glycine than in water. Knowledge concerning the activity coefficients of strong electrolytes in the presence of amino acids would be valuable, however, in the determination of dissociation constants for amino acids themselves, it being necessary to calculate from the measured hydrogen-ion activity what concentration of free hydrogen or hydroxyl ion is present. Some assumption as to activity coefficients is therefore required. For example Birch and Harris[3] assumed γ_{H^+} and γ_{OH^-} to have the same value as in an ampholyte-free solution of identical salt concentration.

Experimental

The thallous chloride used in this investigation was a c. p. preparation recrystallized from distilled and from conductivity water. Theoretical nitrogen values were found for

[2] Bjerrum, Z. physik. Chem., 104, 147 (1923).
[3] Birch and Harris, Biochem. J., 24, 564 (1930).