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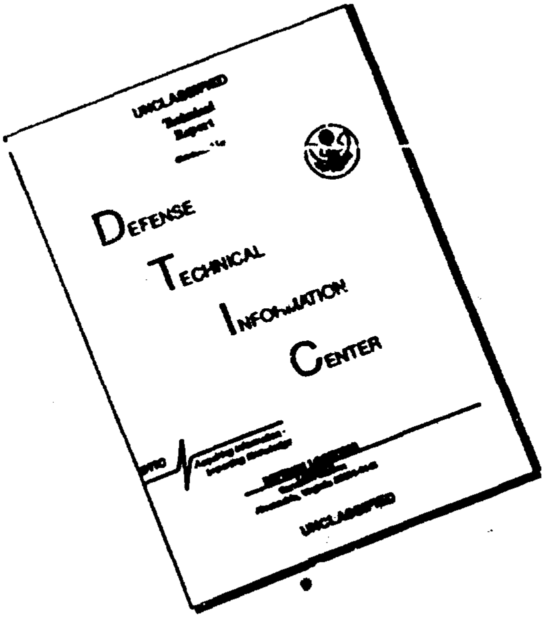

SOME PROBLEMS OF THE CHEMILUMINESCENCE MECHANISM

Trudy Moskovskogo obshchestva
ispitateley prirody (Transactions
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1. This symposium is summing up the initial results of investigations of super-weak luminescence observed in many biologic systems. Just recently, to what this luminescence was connected was unclear: either it reflected specific processes of vital activity, or it was a live system which only played the role of a "thermostat" maintaining at a specific level the chemical reactions which are nonspecific for the organism.

The correlations demonstrated in some reports attest to the connection between the principles of luminescence and vital activity. This enables us to hope that with time bioluminescence will become a fine and effective physical method of studying biologic processes. It is necessary to have in mind, however, that the process of formulating a method will hardly be a speedy and easy matter. And it seems to me that, in so doing, the experience gained in the investigation of chemiluminescence in simpler, purely chemical systems will be as useful in the final analysis as the experience accumulated in the investigation of even simpler systems - - gas-phase systems.

Our report (Allabutayev et al., 1963) considered methods of identifying excited states in the specific reaction of hydrocarbon oxidation - - a reaction which was a convenient model for investigating liquid-phase chemiluminescence. Now, I would like to dwell on a number of general problems bearing on the chemiluminescence mechanism.

2. In different reactions, the nature of excited states may vary.

However, it is possible to assert that at least for the observable and ultraviolet bands of the spectrum the electron state is the excitation bearer, since oscillatory excitation is quickly lost in liquids.

The structure of the spectrum is determined by the luminescent properties of the excited state, and not by the amount of released energy (the energy, it goes without saying, must be no less than the emitted light quantum). For example, in the oxidation of ethylbenzene and methylethylketone a uniform amount of energy is released in the reactions of recombining the overoxidated radicals (110-120 large calories per mole); however, the chemiluminescence maximums fall within the range of 440 millimicrons (65 large calories per mole) and 520 millimicrons (55 large calories per mole), a situation which is connected with the various locations of the levels of the excited products - - acetophenone and diacetyl. Therefore, the presence in the chemiluminescence spectrum of several maximums does not necessarily attest to the parallel occurrence of several chemiluminiscent reactions with different thermal effects.

3. In those cases in which the products of an exothermal reaction have a triplet level, its excitation is certainly conduced by the fact that it is located lower in the majority of molecules and requires less energy than the excited singlet level. The triplet nature of emitters was recommended for chemiluminescent reactions of luminol and lucigenin (lyutsigenin) oxidation (White, 1961, and Kapryakin, 1959, respectively). On the other hand (Rid, 1960) argued against the involvement of triplet states: the spectrum of luminol chemiluminescence was a mirrorlike reflection of the absorption spectrum, which was determined by the lower singlet state. These arguments appear inadequate, since there are well-known cases in which the spectrum of absorption and luminescence is approximately mirrorlike, but connected to the levels of varying multiplicity. For example, upon absorption aldehydes and ketones convert to the singlet level, and luminescent conversion occurs from the triplet state (Yermolayev, 1956).

The quantum yield of luminescence upon the oxidation of luciferin (lyutsiferin) has been recently determined (Seliger, McElroy, 1960). The high significance of the yield - - 0.88 photon per oxidized molecule - - demonstrates that in the given case the excited state is obviously singlet.

4. The problem bearing on the multiplet of an excited particle at times may be clearly solved on the basis of the rule of the conservation of a system's total spin (Wigner's rule). Such an approach has produced results in the investigation of many gas reactions (Kondrat'yev, 1958). Wigner's rule is of assistance in selecting the most probable path from several possible reaction paths. This rule may be formulated in the following manner: if the initial and terminal states of a system do not have uniform values of the total spin quantum number, then transitions between such states must be very unlikely; in case of a complex reaction, other elementary processes prevail over them - - processes for which there are uniform values of the resulting spin in the initial and terminal

states (Kondrat'yev 1958). Wigner's rule has been observed, for example, in reactions of hydrocarbon oxidation investigated by us (Allabutayev et al., 1958) for all conceivable combinations of a multiplicity of original reagents and products:

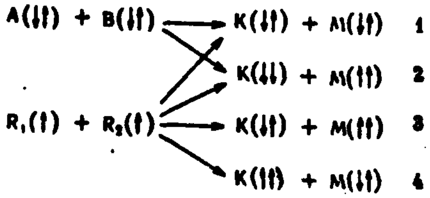
$$RO_2(\uparrow) + RO_2(\uparrow) \rightarrow \overset{\text{alc}}{\text{спирт}}\begin{pmatrix}\uparrow & \uparrow \\ \downarrow & \uparrow\end{pmatrix} + \overset{\text{ketone}}{\text{кетон}}\begin{pmatrix}\uparrow & \uparrow \\ \downarrow & \uparrow\end{pmatrix} + O_2\begin{pmatrix}\uparrow & \uparrow \\ \downarrow & \uparrow\end{pmatrix}$$

total spin or
(суммарный спин: 0 или 1)

total spin or
(суммарный спин: 0, 1, 2 или 3)

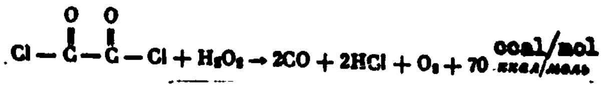
Therefore, products can be obtained both in a triplet and in a singlet state. The fact that triplet acetophenone is the chemiluminescence emmitter in the oxidation of ethylbenzene is linked almost exclusively to a property of this substance which makes for rapid conversion from the singlet to the triplet state. Both states are apparently settled in the reaction. Observed in methylethylketone oxidation are conversions from both the triplet and the singlet states, and the spectrum mirrors the spectrum of the photoluminescence of diacetyl (Vasil'yev, Rusina, 1964). This spectrum is a mixture of fluorescence and phosphorescence (Bäckström, Sandros, 1960).

When applying Wigner's rule, it is necessary to keep in mind that it is applicable to an elementary act, and not to a gross reaction. For example, when the reaction between the saturated molecules A and B occurs in a single elementary act, both products K and M must be obtained either in the singlet or the triplet state (1) and (2). When the reaction proceeds in a radical manner, other combinations are possible (3) and (4).



In view of what we have said, the conclusions of some authors relative to a multiplicity of excited states in a number of chemiluminescent reactions are premature.

For example, Chandross (1963) proposes the formation of a triplet excited product through the interaction of hydrogen peroxide and oxalylchloride:



$$Cl-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Cl + H_2O_2 \rightarrow 2CO + 2HCl + O_2 + 70\ \overset{\text{ccal/mol}}{\text{ккал/моль}}$$

on the basis that O_2 is a triplet molecule and the original reagents are singlet (2). It is clear that if this reaction proceeds in a more complex manner (via the radicals), then other combinations can be realised.

For these same reasons White's conclusion (1961) relative to the triplet nature of the emitter in luminol oxidation is inaccurate - - all the more so since the author himself considers this reaction to be radical.

5. A reaction may proceed even in violation of Wigner's rule, since it is not very strict.

In this case, the excitation process must have a low probability (low yield). And vice versa: if a high yield of chemiluminescence is obtained in a test, then it is rather difficult to expect that the elementary act of excitation will proceed with a multiplet change. That is why, in investigating the chemiluminescence mechanism, it is important to measure exactly the quantum yield of luminescence. In this connection, it is necessary to comment on two widespread errors encountered in works on chemiluminescence.

a. Authors do not always take into account the fact that it is necessary to relate luminescence intensity not to the speed of the gross reaction, but to the speed of the formation of that product which serves as an emitter. For example, in the low-temperature gas-phase oxidation of acetaldehyde, it was found (Topps, Townsend, 1946) that on the average 1 photon is emitted per 10^6-$3 \cdot 10^6$ molecules of acetaldehyde. It would seem that that is a very low yield. However, if one takes into account (as the authors of the work themselves have done) that formaldehyde serves as the emitter and is formed by a factor of 10^4 less than other products, then the yield appears sufficiently high - - on the order of 10^{-2}.

b. Authors do not always take into account the fact that the chemiluminescence process proceeds in two stages and that the total yield of chemiluminescence depends on the excitation yield $\eta^{\text{excl.}}$ and on the emission yield η_{ρ}, respectively (Allabutayev et al., 1963). These quantities have a completely different physical significance and dissimilarly depend on molecular structure, environment, test conditions, etc. For example, in the above-mentioned case, the yield 10^{-2} does not mean that in the reaction 1 excited molecule is formed per 100 nonexcited molecules of formaldehyde. As Geydon has commented in a discussion about the work of Topps and Townend (1946), excited formaldehyde can be effectively quenched under test conditions (i.e., $\eta_{\rho} \ll 1$), and it can possibly be formed in the reaction with a 100-percent yield (i.e., $\eta^{\text{excl.}}_{\rho} \approx 1$).

6. Some authors are developing notions concerning the radical character of chemiluminescent reactions (White, 1961). Moreover, they consider the existence of luminescence to be proof of the participation of radicals in a reaction (Rostorfer, Cormier, 1957; Behrens et al., 1963) and even insist that chemiluminescence in the short-wave (blue and shorter) band can be the result only of a reaction with the participation of two free radicals. This conclusion was presented in an article by Bremer (Bremer, Friedmann, 1954). This piece, treating chemiluminescence as a reversed photochemical reaction, examined the elementary processes capable of being accompanied by chemiluminescence and presented examples. In fact, the effective conversion of chemical energy into radiation is more probable and must be encountered more frequently in the recombination of radicals than in other, less exothermal processes. It would be nevertheless inaccurate, in principle, to deny the possibility of excitation even in reactions differing from the recombination variety. For example, intense flashes have been observed upon the introduction of molecular fluorine into a jet of H_2 or CH_4 (Kapralova et al., 1963). In these reactions are the following elementary acts:

$$H + F_2 \rightarrow HF + F + 100 \text{ ккал/моль, ccal/mol}$$
$$CH_3 + F_2 \rightarrow CH_3F + F + 70 \text{ ккал/моль. ccal/mol}$$

They are quite exothermal but include one free radical as an original agent.

In our view, there exist only two conditions necessary for the appearance of chemiluminescence:

a) the reaction must be sufficiently exothermal (the law of the conservation of energy);

b) the product must have an adequate level of energy, the emission from which product takes place with sufficient probability.

The nature of the reaction (radical, ionic, molecular) is of no significance. Correspondingly, the fact itself of the existence of chemiluminescence does not necessarily point out the radical mechanism of a reaction, although in a majority of known cases (including those investigated by us) luminescence is nevertheless excited when radicals are recombined.

7. Chemiluminescence is a very specific phenomenon, and the conversion of the chemical energy into light energy in various reactions may take different paths. Moreover, not one but several products can be excited in the same reaction; they may emit either in the same or in various spectral bands. For example, in the oxidation of hydrocarbons there are formed, besides the ketones emitting in the blue band, excited oxygen molecules, whose emission falls into the red band (Vasil'yev, Rusina, 1964).

In individual reactions, a great role can be played by secondary processes - - the quenching and transfer of energy (Allabutayev et al., 1963; Vassil'yev, 1962; Vasil'yev, Rusina, 1963). In each case, identification of the excited states should be based on an exhaustive experimental study, which would include the obligatory consideration of the chemical mechanism of the reaction and the secondary physical processes.

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