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DISCUSSION

On the “Spatially Separated Ion Pair”

I. M. Serebryakov

Donetsk National University, Universitetskaya St. 24, Donetsk, 83055 Ukraine
e-mail: serebryakov@dn.farlep.net

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Abstract—The proof of existence of a new intermediate, the “spatially separated ion pair”, in the pathway of unimolecular heterolysis of organic compounds is critically analysed. It is concluded that the existence of this intermediate is not proved.

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Dvorko et al. [1] suggested an additional intermediate in the Winstein’s heterolysis scheme, the “spatially separated ion pair.” In all subsequent studies the authors interpreted their experimental data using their expanded scheme. The discovery of a new intermediate in a classic reaction is an important event. However, to our knowledge, in the literature the validity of the hypothesis advanced by Dvorko et al. was never analyzed. Similarly, the concept of “spatially separated ion pair” was not used by other researchers to interpret their data. In our opinion, it is time to assess the grounds of this hypothesis.

The transformation of a contact ion pair into the solvent-separated pair, according to Dvorko et al. [1], proceeds as follows. The nucleofuge moves into a nearby cavity between the solvent molecules in the nonequilibrium solvation regime, that is, the reorganization of the solvation shell lags behind the nucleofuge transfer. After the actual transfer is complete, a partially desolvated solvent-separated ion pair is formed, which was named by the authors “spatially separated ion pair.” This new intermediate then is solvated to reach equilibrium, and thus it is transformed into a solvent-separated ion pair. The lifetime of the “spatially separated ion pair” is determined by the solvent relaxation time, about 10–100 ps, which, according to the authors, is sufficient for the particle to operate as an intermediate [2].

According to Dvorko et al. [3], the existence of the “spatially separated ion pair” was confirmed by a series of quantum-chemical calculations. However, only in one of the papers [4] referred to by the authors, three minima were found on the calculated energy profile, as it should be if an additional intermediate was formed. The accuracy of these calculations is rather doubtful as only 14 solvent molecules were included. In other papers [5–7], the number of ion-pair inter-mediates was 2 or 1. The structure of the “spatially separated ion pair-like” intermediate, allegedly described in [5], in fact corresponds to the solvent-separated ion pair with one layer of appropriately oriented water molecules between the ions. Moreover, in this paper the quasi-static picture of heterolysis was considered, that is, the model of equilibrium solvation at all points of the reaction coordinate was used. However, the “spatially separated ion pair” by the authors’ definition can occur only in the non-equilibrium solvation regime. Generally speaking, at present the results of quantum-chemical calculations for such complex systems can hardly be accepted as a convincing argument. Therefore let us turn to the analysis of experimental data presented by the authors.

Dvorko et al. presented two arguments for the need to include an additional intermediate in the Winstein’s scheme. The first one is based on the analysis of salt effects in the reactions of unimolecular heterolysis studied using the verdazyl method of monitoring developed by the authors. The logic of this argument is as follows [8, 9]:

(i) In aprotic solvents in the course of unimolecular heterolysis free carbocations are not formed.

(ii) The presence of salts can only increase the rate of the contact ion pair separation.

(iii) Triphenylverdazyls react irreversibly only with the solvent-separated ion pairs, and in the absence of salts they capture this intermediate quantitatively. In other words, triphenylverdazyls are indicators for the solvent-separated ion pair.

(iv) In the presence of salts (mostly chlorides), in some cases the heterolysis rate of substrates RX depends on the substituents in the indicator and its concentration. This is ascribed to the competition of the verdazyl and the salt anions for the solvent-separated ion pairs. With increasing concentration of the indicator the observed reaction rate increases reaching a plateau, but it is still lower than the reaction rate in the absence of the salt. In the saturation region, verdazyl captures all the solvent-separated ion pairs. Since the negative salt effect can not be brought about by the action of the salt on the contact ion pair [statement (ii)], it remains to assume that the salt impacts “negatively” on another intermediate preceding the solvent-separated ion pair, i.e. on the “spatially separated ion pair”.

We will not contest here the validity of the statements (i) and (ii), although we think that the latter is only the authors’ opinion without any good grounds.[1] The third statement, according to our data, is incorrect. We have previously shown that triphenylverdazyls do not capture to a notable extent *any* ion pairs of benzhydryl bromide in any of studied aprotic solvents [10, 11]. Unfortunately, the authors of the hypothesis at that time chose not to discuss this issue. Later we showed that verdazyls also do not capture any ion pairs of 1-adamantyl picrate in acetonitrile both in the presence and in the absence of different salts. The observed dependence of the verdazyl consumption rate on its concentration and structure was shown to be the result of the equilibrium shift in the reaction of the indicators with acids caused by the relatively basic chloride anions. The true rate of the substrate heterolysis does not depend on the concentration or the structure of the indicators [12]. The faulty of the third statement means the uselessness of any further analysis. This fact also voids the grounds of the extremely detailed schemes of the salt effects proposed by the authors, since they are based on the assumption (iii).

The other evidence for the “spatially separated ion pair” is the “negative effect of nucleophilic solvation.” According to Dvorko et al., in some cases the rate of unimolecular heterolysis of substrates RX decreases with increasing the nucleophilicity of the solvent. This, according to the authors’ logic, confirms the described above pattern of the contact ion pair separation, since otherwise it would be difficult to find an explanation for this effect. In the preceding paper [13] we came to the conclusion that the operation of the “negative effect of nucleophilic solvation” in the considered reactions is at least questionable.

In principle, we do not object to the picture of the contact ion pair separation drawn by the authors. Problems arise when considering the properties that the “spatially separated ion pair” has to exhibit according to the considered hypothesis.

A key property of the “spatially separated ion pair” is its ability to interact with salts. This interaction hardly can be proved at the macro level. For example, if an increase in the solvent ionic strength promotes the separation of the contact ion pair, it is likely to stabilize the “spatially separated ion pair,” rather than contribute to its collapse. Thus, the effects of the salt on both intermediates with respect to the observed reaction rate can be unidirectional, and at present we can not see the way to prove the action of the salt exactly on the “spatially separated ion pair.”

Let us turn to the micro level. If the contact ion pair before its separation was aggregated with the salt ions, by analogy with the above it is unlikely that we can distinguish the net effect of the salt on the “spatially separated ion pair.” If the pre-association was not noticeable, then how can the salt get involved into the interaction with the “spatially separated ion pair?” During the life-time of the “spatially separated ion pair” neither the carbocation nor the ions of the salt can shift significantly as the ion diffusion proceeds slower than the resolvation of the already formed “spatially separated ion pair.” The collapse of the “spatially separated ion pair” to form the contact ion pair could occur from the collision of the nucleofuge with the salt anion, but the probability of such event is very low.[2]

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[1] Formation of the complex of the salt with the contact ion pair, probably decelerates the recombination due to the Coulomb stabilization. But in the same way the salt can slow down further separation of the contact ion pair, so the overall effect is unpredictable.

[2] If in 1×10^{-2} M solution the salt exists in the form of free ions or ion pairs that are not associated with the carbocation, the average distance between the carbocation and the neighboring salt anions will be about 40 Å (for the space centered model). If the salt ions in solution form larger aggregates, the average distance between them and the carbocation will be even greater.

If, nevertheless, the “spatially separated ion pair” does react with salts, it remains unclear why this intermediate does not react with verdazyls.

According to the authors’ theory, the rate constant of the reaction of the solvent-separated pair with verdazyls is 50–100 times higher than with azide or chloride ions [8], and at verdazyl concentration by two orders of magnitude below the concentration of the salts we can observe their competition for the solvent-separated pair. Why the “spatially separated ion pairs” do not take part in the reaction? We can imagine two reasons for that:

(a) the “spatially separated pair” reacts with verdazyls much slower than the solvent-separated pair;

(b) the “spatially separated pair” reacts with salts much faster than the solvent-separated one.

Both these assumptions are unlikely. The “spatially separated ion pair” is a destabilized solvent-separated pair, thus we can expect its greater reactivity towards both reagents. On the other hand, the reaction of benzhydryl chloride cationoids, and hence of the corresponding solvent-separated pair, with chloride ions in acetonitrile is diffusion controlled [14]. To implement the assumption (b), the “spatially separated ion pair” should react with chloride ions at rates above the diffusion limit. For the reaction with salts such reactivity cannot be explained by the “outer-sphere electron transfer,” by which, according to the authors, the solvent-separated pairs exhibits fantastic rate constants in their reactions with verdazyls.

We believe that the available experimental results can be satisfactorily explained by the following scheme: verdazyls react with the acid that is the end product of the substrate solvolysis, while the salts act on the contact and (or) on the solvent-separated ion pair (apart from the salt effects on the substrate ionization and on free carbocations if they are formed). Thus, the Winstein scheme does not require any expansion.

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