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# THE NATURE OF THE "CHANNEL 3" DECAY MECHANISM IN BENZENE

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A simple but realistic mechanism for the "channel 3" decay in benzene is proposed where energy levels of isomers are incooporated as intermediate states of $S_1 \rightarrow S_0$ internal conversion.

Although many theoretical and experimental studies have been devoted to account for the anomalous radiationless transition in benzene, no completely satisfactory description seems to have emerged.[1] The most typical situation in this anomaly is the fact that the radiationless transition rate rises by a factor of $10^3$ in an energy interval of only 400 $cm^{-1}$,[2] and this is ascribed to the unknown "channel 3" mechanism.

The mechanisms having been proposed to explain this anomaly can be roughly classified into two groups: (1) those which involve photochemical reactions and (2) $S_1 \rightarrow S_0$ internal conversion (IC) with extremely large dependence on the excess energy. Although predissociation (to give rise to formation of phenyl radical and H atom) or "preisomerization" (to give rise benzvalene, fulvene or else) can be picked up as a candidate for the reactions in mechanism (1),[3] they do not seem to be well accepted because of the only few clear evidences of the reaction products.[4] For example, Lee et al.[4b] have actually detected benzvalene as a product but failed to determine the quantum yield of the isomerization which has to be at least 0.1 at shorter wavelengths, e.g. 250 nm, to be consistent with their argument. The quantum yield 0.18 estimated by Lutz et al.[4a] for the formation of benzvalene from benzene in cyclohexene irradiated by 253.7 nm light, which was a little too big to be consistent with the result in vapor phase, might be taken to support their conjecture. However, it can be done only apparently because solute-solvent interaction can significantly influence the coupling scheme in radiationless transitions as is indicated in Fig. 1 (vide infra).

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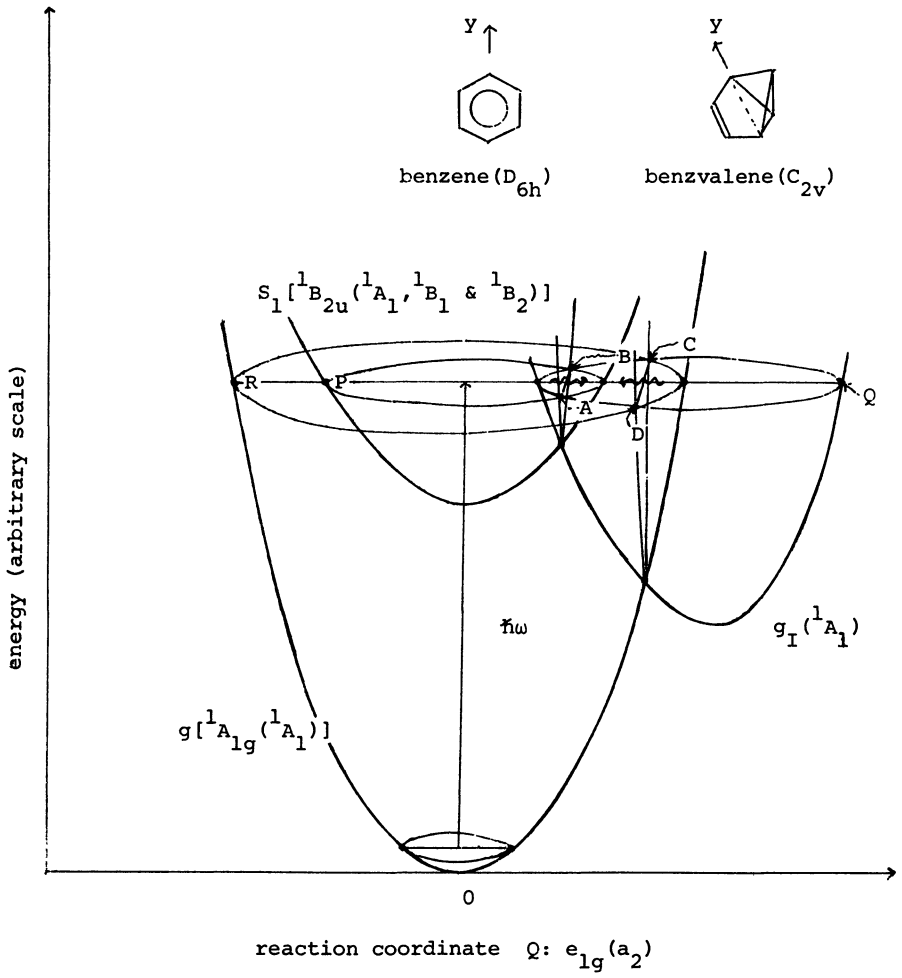


Figure 1. Schematic diagram for the channel 3 decay of benzene. An optically prepared state (DBO type vibronic state) shown by circle PAB decays into isoenergetic ground vibronic states RCD through ground vibronic states ABCQD of the isomer, resulting in rapid IC as fast as $\gtrsim 10^{11} s^{-1}$. The reaction coordinate consists most likely of $e_{1g}(a_2)$ out-of-plane vibrations of benzene (benzvalene), while coupling modes are supposedly, for benzvalene, out-of-plane type $a_1$ vibrations to which several vibrational modes of benzene are correlated.

As for the latter mechanisms (2), we have to admit some accidentals like extreme closeness[5] or even crossing of $S_1$ and $S_0$ levels and furthermore involvement of the third levels.[6] Therefore, these proposals may not be well accepted because of the lack of reality, i.e. good correlations with the experimental findings.

Instead of discussing[7] the disadvantages (and advantages) of the above proposals, a new mechanism for the channel 3 decay of benzene will be presented. The relevant mechanism is just a combination of the two series of proposals and is illustrated in Fig. 1. The potential surfaces in this figure are for the states indicated in diabatic Born-Oppenheimer (DBO) approximation[8] which seems to be more suitable than adiabatic BO(ABO) approximation to explain the experimental (spectroscopic) observation. By this diagram, the decay of $S_1$ state in benzene at higher excess energies (>3000 $cm^{-1}$) can be interpreted as an $S_1 \rightarrow S_0$ IC involving $S_0(g_I)$ state of benzvalene as an intermediate state. The perturbing term for this transition is, of course, a residual term of the exact molecular Hamiltonian minus the molecular Hamiltonian in DBO approximation and might be further partitioned into vibronic coupling and anharmonic coupling terms. In other words, the DBO wavefunctions defined here can be taken to be fairly close to crude BO(CBO) wavefunctions.[9] So, this situation may be rather described as a strong (electron-phonon) coupling case.[9,10] Thus what happens after the absorption of a photon $h\omega$ is just an isoenergetic $S_1 \rightarrow S_0$ IC through isomer level (in the description of kinetics). Therefore, it is not essential of the isomer to be produced although the production may have some contribution. This description is quite different from the mechanism proposed by Lee et al.[4a] because their intermediate is an actual (chemical) one to be observed experimentally. Since the excited level is assumed to be above the crossing points (surfaces) of DBO potential surfaces, the decay rate is expected to be extremely fast ($\gtrsim 10^{11} s^{-1}$). The same mechanism is still expected to work even at lower excess energy ($\simeq$3000 $cm^{-1}$) because $S_1$ levels of benzene and $S_0$ levels of benzene may be continuous above the ABO potential surface. Therefore, if described on ABO basis, vibrational energy redistribution (VER)[9] seems to work as a rate determining step in this energy region giving rise to suitable explanation of the energy dependence (and mode dependence). The reasons why benzvalene was chosen rather than the other isomers are both experimental and theoretical.[7] For example, the potential surface of fulven does not seem to cross the $S_1$ surface of benzene at lower energy because its minimum seems to be far apart from that of $S_0$ on the reaction coordinate.[3] Another reason may be found in the fact that, for this mechanism, some out-of-plane modes can constitute the reaction coordinate and consequently some other

out-of-plane modes can work as good coupling modes between $S_1(S_0)$ state of benzene and $S_0$ state of benzvalene in conformity to the experimental and theoretical evidences such as spectroscopic data.[11]

Finally, the differences (as well as similarities) between the present mechanism and some of the previous mechanisms will be briefly discussed. The mechanism proposed by Formosinho et al. looks similar to the present model (See their Fig. 1.). However, their potential surface of quasi-dissociated benzene does not cross with $S_0$ surface of benzene and furthermore there is no experimental evidence to support that conjecture. Not much can be discussed about the theoretical works mentioned above[5] because they are just pointing out the possibility and cannot be used to disprove the other possibilities judging from the current status of the theoretical study for the "quantitative" discussion of the radiationless transitions. The work by Fischer et al.[6] which appeared while the present study was in a final stage is fairly close to this work except for that the third state which must have suitable coupling with $S_1$ and $S_0$ states of benzene was not identified in their paper.

More detailed arguments in favor of this mechanism against the others will be published elsewhere[7] by taking account of various experimental and theoretical data related to this problem.

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