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CAGE EFFECT IN RECOIL STUDIES*

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ABSTRACT

The role of cage effect is one of the most discussed questions of hot atom chemistry in condensed organic systems. So far no direct evidence is available for assessing the exact contribution of thermal recombinations occurring in the liquid cage to the stabilization processes of recoil atoms. However, some conclusions can be drawn from experimental observations concerning the influence on product yield of hot atom recoil spectra, the effects of density, phase and long range order of the medium as well as from comparing systems providing cage walls of different chemical reactivities towards the recoil atom.

Recent developments in this field are reviewed primarily based on the investigations of recoil halogen reactions in aliphatic and aromatic hydrocarbons and their haloderivatives.

АННОТАЦИЯ

Роль эффекта клетки является наиболее спорным вопросом в области химии горячих атомов в конденсированных органических средах. До сих пор не удалось непосредственно определить вклад термической рекомбинации пар радикалов в процессы стабилизации атомов отдачи. Некоторые выводы могут быть сделаны на основе изучения влияния плотности, агрегатного состояния и дальнего порядка системы на выход продуктов стабилизации. Дальнейшая информация может быть получена на основе сравнения систем с различной реакционной способностью молекул, составляющих стенку жидкой клетки. Представлен обзор новейших результатов в этой области, исходя, главным образом, из исследований реакций атомов отдачи галогенов с алифатическими и ароматическими углеводородами, а также с их галогидными производными.

KIVONAT

A kalitkahatás szerepe a kondenzált fázisu szerves rendszerek forrátoatom-kémiájának legtöbbit vitatott problémái közé tartozik. Eddig még nem sikerült közvetlenül kimutatni, milyen mértékben járul hozzá a kalitkán belüli termikus rekombináció a visszalökött atomok stabilizációs folyamataihoz. Bizonyos következtetések levonhatók azokból a kutatásokból, amelyek a sűrűség, halmazállapot és hosszútávú rendezettség hatását vizsgálják a stabilizációs termékek hozamára. További felvilágosítást nyújthat olyan rendszerek eredményeinek összehasonlítása, amelyekben a kalitka falát különböző reakciókészségű molekulák képezik. E terület újabb eredményeit foglaljuk össze, elsősorban a visszalökött halogéneknek alifás és aromás szénhidrogénekben és azok szubsztituált származékaiban végbemenő reakciói tanulmányozása alapján.

The photolytic cage effect was postulated by Franck and Rabinowitsch in 1934 [1], the same year the Szilárd-Chalmers effect [2] was discovered. As if it were symbolic the problematics of cage reactions, their role in the stabilization processes of recoil atoms has accompanied the hot atom studies of condensed phases ever since.

In the liquid phase the recombination of a radical pair generated in the same event is greatly enhanced if we compare it with the gas phase. This is the result of interactions with the solvent molecules which interfere with the escape of the fragments after dissociation from each other's vicinity. That is, the only important property of the loose term "cage", is the temporary prevention of separation by diffusion of a geminate radical pair.

In the early fifties Noyes [3,4] and later Hamill with his coworkers [5] introduced geminate radical recombination as a more precise term for this phenomenon. They also suggested that a distinction be made between the two different types of these processes.

In primary geminate recombination the fragments remain in close proximity - almost within bonding distance of one another - until they lose enough energy to recombine. This takes place in a period of 10^{-13} - 10^{-12} s, not much longer than the time order of vibration.

Secondary geminate recombination is diffusive in nature: the initial separation of the fragments is greater than the molecular diameter and they do interact with the solvent molecules before they re-encounter and finally recombine with the original partner. The time scale for this process was assumed to be of 10^{-11} - 10^{-10} s (10-100 ps). Indeed it has been found recently by Eisinger and his colleagues [6] - using the picosecond laser technique - to be

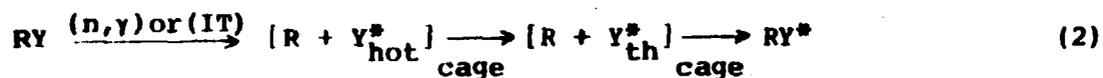
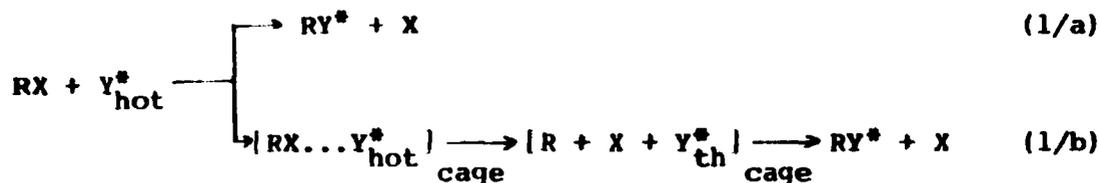
of about 70 and 140 ps for I_2 recombination in hexadecane and CCl_4 , respectively.

Radicals which survive over a period of about 10^{-9} s almost certainly diffuse so far apart - escape the cage - that there is only a negligible chance for them to re-encounter each other. They will react with other radicals or molecules of the bulk substance at random and will, therefore, be directly affected by small amounts of scavenger present. This offers a good chance to distinguish between reactions of uncorrelated - kinetically free radicals and cage processes.

On the other hand it has proved difficult if not impossible to distinguish experimentally between the results of primary and secondary geminate reactions despite the conceptual distinction suggested by Noyes [4]. According to this, primary recombination occurs too rapidly for surrounding molecules to compete with it, except in a medium consisting almost entirely of a very reactive scavenger. In contrast, secondary processes should be influenced by the changing reactivity of the medium since they do involve interaction of the fragments with the solvent molecules.

A more sophisticated picture of cage processes was revealed by trajectory studies - first of all by Bunker and Jacobson [7]. However, in recoil studies even the questions raised by the qualitative picture described above can not always be answered unequivocally.

The problem we face in condensed phase hot atom chemistry is to distinguish between reactions which lead to similar products although they are different in nature [8,9]; i.e. between genuine hot processes (Eq. 1/a) and reactions of thermalized recoil atoms (Y_{th}^*) with the nearby radicals (R). These radicals may be originated from the previous attack of the hot recoil atom (Eq. 1/b). Or, radioactive atoms with relatively low recoil energy may recombine in the cage with the parent radical (Eq. 2). Recent developments in this field are based primarily on studying the effect of density, phase and the reactivity of the medium on the stabilization processes of recoil halogens.



Density variation technique

At first sight, the most straightforward approach to this problem is to study the influence of continuously increasing density on the products of recoil atoms.

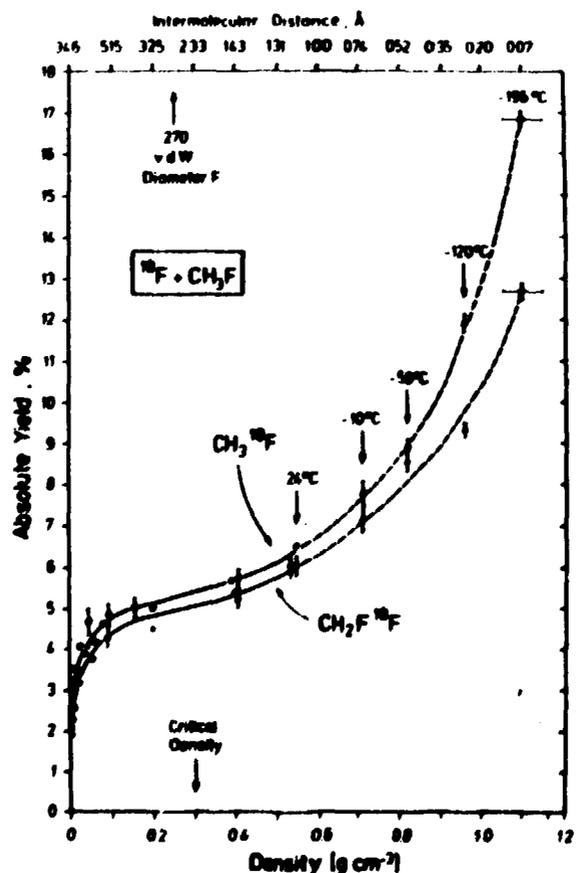


Fig. 1. Absolute yields of substitution products as a function of density in the $\text{CH}_3\text{F} - \text{I}_2$ system
 o: CH_3^{18}F ; \blacktriangle : $\text{CH}_2\text{F}^{18}\text{F}$ [10]

Figure 1 shows the well known plot established by Richardson and Wolfgang [10] for the F and H replacement by recoil ^{18}F atoms in CH_3F . It was interpreted as reflecting at lower pressures the growing collisional stabilization of internally excited hot products while demonstrating the onset of cage recombinations above critical density.

Similar dependence has been established for several recoil halogens reacting in volatile aliphatic substrates in a number of laboratories - as listed in Table 1. The interpretation of the results, however, was not always the same.

Table 1
Density variation studies of cage reactions

Recoil atom	System	Ref.
^{18}F	CH_3F	10
^{18}F	CF_3CH_3	19-21
^{18}F	CHF_2CH_3	19, 20
^{38}Cl	meso- and rac- $(\text{CHClF})_2$	18
^{80}Br , $^{82\text{m}}\text{Br}$, ^{82}Br	CH_3X ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$)	12
^{80}Br , ^{82}Br	C_2H_6	13
^{123}I , ^{128}I	CH_4 , C_2H_6	11, 14
^{128}I	C_2H_2	15
^{128}I	propyne	16
^{128}I	1- and 2- C_4H_6	17

Thus, Machulla and Stöcklin [18] suggested that a "caged complex" is formed, i.e. a single intermediate whose lifetime is prolonged by the high density of its surrounding medium. They attribute the higher yields measured in liquid phase to this intermediate instead of to radical pair recombination.

Manning and Root [19-21] have found that the extent of collisional stabilization of internally excited hot products changes over the same range as that of cage recombination. Therefore, as they pointed out, reliable establishment of cage reactions can be performed from density variation experiments only if combined with a total yield analysis for every particular hot reaction channel. Applying this method they could show that some products are formed to a significant extent in cage processes whereas others are not. An example for ^{18}F atoms reacting in CH_3CF_3 system [20] is shown in Fig. 2.

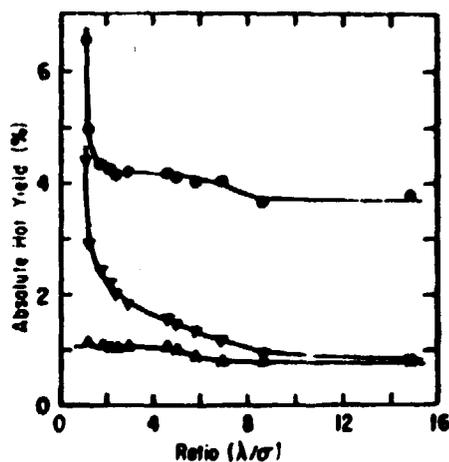


Fig. 2. Total mechanism plots for ^{18}F -for-F and ^{18}F -for- CH_3 reactions in CH_3CF_3 .
 ●: total ^{18}F -for-F yield; ▼: ^{18}F -for-F yield corrected for excitation decomposition;
 ▲: total ^{18}F -for- CH_3 yield [20]

The yields of F and CH_3 replacement by ^{18}F atoms are given as a function of reduced length parameter, i.e. the ratio of mean intermolecular distance (λ) to the molecular diameter (σ). It can be seen that with decreasing λ/σ ratio, i.e. with increasing density, the apparent F-replacement yield (middle curve) continually increases whereas that corrected for excitation decomposition channels (upper curve) shows a plateau over a wide range down to values smaller than 2. The sharp rise at this point is attributed to the onset of cage processes. On the other hand, corrected yield for CH_3 -replacement (lower curve) does not show

any increase even at low λ/σ values, thereby indicating the absence of cage reactions. (Plots of similar nature were also obtained by Rack and colleagues for recoil Br and I reacting in methylhalogenides and ethane [12-14].)

The total organic yields due to cage processes have been found to be comparable in extent to the true hot yields in these systems as it is demonstrated by the data in Table 2. Bearing in mind that efficient H-abstraction by thermal F atoms from the parent molecules successfully competes with the secondary processes these yields were attributed to primary geminate recombination.

Table 2

Contribution of hot and cage recombination processes to the organic yields in fluorinated ethanes [20]

System	Organic yield (%)	
	Hot	Cage (primary)
$^{18}\text{F}/\text{CF}_3\text{CH}_3$	8.9	4.0
$^{18}\text{F}/\text{CHF}_2\text{CH}_3$	8.6	5.6

Variation of medium reactivity

Another widely used method to study the role of cage processes is by altering the reactivity of the medium towards the thermalized recoil atoms. For example, in dilution experiments applying solvents of different reactivities, we can change the competition between secondary cage recombinations of recoil atoms with original fragments and their reactions with the solvent molecules of the cage wall.

Brinkman [22,23] together with his colleagues recently performed a comprehensive study on recoil Cl atoms reacting in a series of halocarbons diluted with solvents of different reac-

tivities. Comparing the results with those of radiolytic studies they came to the conclusion that e.g. in Cl-methanes and Cl-ethanes only about 3-5% of the total activity can be attributed to hot products whereas much higher yields of about 20-30% to the products of cage reactions [22].

We made an attempt to establish the role of cage reactions for recoil Cl atoms in liquid dichlorobenzenes (DCB) [24]. For this purpose we compared the effect of different solvents present in high concentrations with the effect of a reactive scavenger present in small concentration.

The results are summarized in Table 3. They show a drastic decrease in Cl-replacement yield if the parent DCB molecules in the cage are substituted by molecules highly reactive towards thermalized ^{38}Cl atoms such as e.g. aliphatic hydrocarbons and alcohols. The addition of I_2 scavenger has no effect in these cases.

Table 3
Effect of diluents on the yield of $o\text{-C}_6\text{H}_4\text{Cl}^{38}\text{Cl}$ [24]

System	Diluent mole%	Yield (% of total activity)			
		no I_2	+0.5 mole% I_2	Corr. for dilution	
$o\text{-C}_6\text{H}_4\text{Cl}_2$	0	30.5	15.7	15.7	
	- C_6H_{12}	90	1.3	1.3	13
	- CH_3OH	90	1.9	-	19
	- $\text{C}_2\text{H}_5\text{OH}$	90	1.2	-	12
	- C_6H_6	90	15.2	2.0	20
	- $n\text{-C}_7\text{F}_{16}$	98	36.2	-	-
	- C_6F_6	90	40.0	8.2	82

Dilution with benzene - aromatic hydrocarbon where hydrogen abstraction is an endothermic process - has a much less dramatic effect. The addition of I_2 scavenger, however, decreases the yield to approximately the same value. This phenomenon can be

explained by the formation of a charge transfer [25] π -complex between Cl atoms and benzene which competes with the cage recombination by promoting the escape of ^{38}Cl atoms from the cage [26]. This complex is not stable enough, however, to prevent the ^{38}Cl atoms from reacting with the surrounding molecules and radicals in non-cage reactions resulting in higher yields than expected for dilution. The addition of I_2 scavenger eliminates these bulk reactions.

If we compare the yields corrected for dilution (last column in Table 3), it is obvious that the addition of an efficient scavenger in the usually applied small amounts has essentially the same effect as does a reactive cage wall around ^{38}Cl atoms. It means that in a system promoting the escape of thermalized recoil atoms from the cage the role of secondary geminate recombination cannot be significant.

In contrast, in the systems highly diluted with perfluorinated hydrocarbons, represented by C_6F_6 and $n\text{-C}_7\text{F}_{16}$ in Table 3, the yields do not decrease at all and remain high even in the presence of I_2 scavenger. The enhancement prevails only for the Cl-replacement yields - as can be seen from Fig. 3



Fig. 3. Yields corrected for dilution vs. mole fraction of C_6F_6 in systems $o\text{-C}_6\text{H}_4\text{Cl}_2 - \text{C}_6\text{F}_6 + 0.5$ mole % I_2 [24]

where the lines show the ^{38}Cl -for- Cl and ^{38}Cl -for- F yields corrected for dilution. It seems to be connected with replacing the DCB by the C_6F_6 in the cage. Surrounding the recoil ^{38}Cl by molecules highly inert towards chlorine atoms [27], thereby hindering its escape, consequently increases the probability of recombination with the chlorophenyl radicals. Contribution of the thermal $^{38}\text{Cl} \rightarrow \text{Cl}$ exchange in the liquid cage cannot be excluded either for the aromatic chloro compounds [28]. ^{38}Cl -for- F replacement in the same systems does not change with the composition indicating a genuine hot process.

It is interesting that recent results of dilution experiments coincide with some conclusions drawn in our laboratory a couple of years ago [29]. We then tested the validity of conventional reaction kinetics in the formation of ^{38}Cl labelled products in binary mixtures. Our basic assumption was that these laws should prevail only if the reactants were homogeneously distributed, i.e. if cage processes could be neglected. Using some reasonable approximations we have shown that if the homogeneous kinetics prevails a linear dependence can be found between the reciprocal value of the product yield (R) and the concentration ratio of the two components (C_1, C_2) of a binary mixture (Eqs. 3, 4).

$$\frac{d[R_1]}{dt} = k_1 [C_1] [^{38}\text{Cl}] = k_1 [C_1] \frac{\phi \sigma h}{\sum_{i=1}^L k_i [C_1] + \sum_{j=L+1}^N k_j [C_2]} \quad (3)$$

$$\frac{1}{[R_1]} = \frac{1}{\phi \sigma h} \left(\frac{\sum_{i=1}^L k_i}{k_1} + \frac{\sum_{j=L+1}^N k_j [C_2]}{k_1 [C_1]} \right) = K_1 + K_2 \frac{[C_2]}{[C_1]} \quad (4)$$

where $k_{i,j}, \phi, \sigma, h$ and consequently K_1, K_2 are constants.

As can be seen from *Fig. 4* linear dependence was found for the formation of the major replacement products from the aromatic compounds DCB and $\text{C}_6\text{H}_5\text{NO}_2$ in their mixtures with CCl_4 . On the other hand *Fig. 5* demonstrates a typically nonlinear dependence for the formation of labelled CCl_4 in binary mixtures with alcohols. This might indicate cage effect which would be well in line

with the results of Brinkman and colleagues who found especially high caging yields for labelled CCl_4 [22].

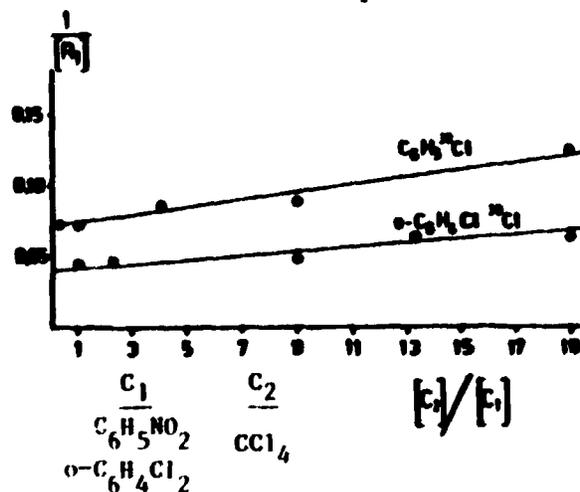


Fig. 4. ^{38}Cl -for-Cl replacement yields vs. composition of the binary mixtures $\text{C}_6\text{H}_5\text{NO}_2 - \text{CCl}_4$ (●) and $o\text{-C}_6\text{H}_4\text{Cl}_2 - \text{CCl}_4$ (○) [29]

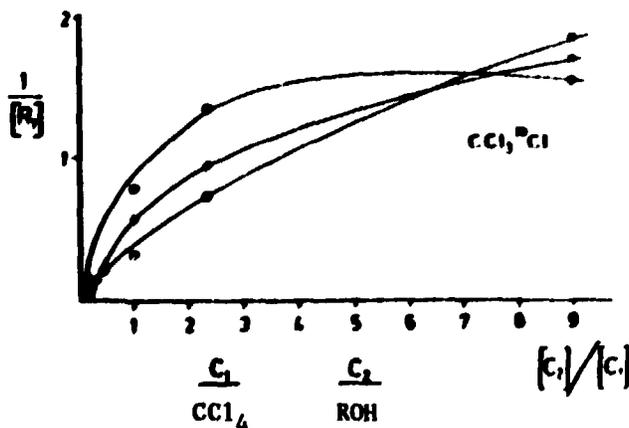


Fig. 5. ^{38}Cl -for-Cl replacement yields vs. composition of the binary mixtures $\text{CCl}_4 - \text{ROH}$. $R = \text{CH}_3$ (x); $n\text{-C}_3\text{H}_7$ (●); $i\text{-C}_3\text{H}_7$ (○) [29]

Experiments with solid phase

Solid organic systems may offer a tool for distinguishing between uncorrelated and geminate radical recombinations, as shown in radiation chemistry [30]. Furthermore, if we take glassy mixtures (where the components are distributed more or less homogeneously) and compare them with the crystalline ones (where the com-

ponents are often separated in clusters) this may provide information on the reactions of radicals with the cage wall.

This fact also seems to have been recognized recently by hot atom chemists. The main difficulty in this field is to perform reliable analysis of the original products of recoil atoms due to limited applicability of "in situ" techniques. Still, lately some phenomena reflecting the specific solid state conditions have been reported.

Rack and coworkers [31,32] have found a surprising constancy of yields for labelled biomolecules over a 100-fold concentration range in frozen aqueous solutions, as shown in Table 4 on the example of diiodotyrosine (DIT) labelled with ^{128}I . In contrast, in liquid mixtures the labelled biomolecule yields decreased according to dilution. This behaviour of frozen systems has been explained on the basis of ice structure where the water molecules are arranged in hexagonal pattern with much empty space in between. The individual biomolecules are trapped in these empty spaces and the recoil ^{128}I atoms recombine with the organic radical in this cage.

Table 4

Absolute product yields of high-energy ^{128}I in liquid and solid aqueous diiodotyrosine [31]

System	DIT, mole %	Products ^a	Absolute yield, %
Liquid DIT at 25 °C	8.2×10^{-3}	I- DIT	$\leq 55.6 \pm 4.0^b$ 19.5 2.4
	8.2×10^{-4}	I- DIT	$\leq 85.1 \pm 3.7$ 7.7 1.7
	8.2×10^{-5}	I- DIT	$\leq 100 \pm 2.1$ 3.2 1.3
Solid DIT at -77 °C	8.2×10^{-3}	I- DIT	$\leq 43.4 \pm 2.1$ 16.9 2.7
	8.2×10^{-4}	I- DIT	$\leq 48.3 \pm 3.1$ 17.0 2.1
	8.2×10^{-5}	I- DIT	$\leq 58.2 \pm 4.6$ 18.6 1.6

^a ^{128}I labeled product; ^b Represents a maximum value.

Similar constancy of parent compound yields has been observed in our laboratory for a number of organic mixtures frozen in the crystalline phase [33] as is shown in Table 5 for dichloroethane (DCE) and dichlorobenzene (DCB) in their mixtures with alcohols. We interpreted this phenomenon by assuming cluster formation where the recoil atoms react with the neat parent substance alone. This assumption seems to be supported by the results obtained for frozen glassy systems of the same composition.

Table 5

³⁸Cl-for-Cl and ³⁸Cl-for-F replacement yields in liquid, glassy and crystalline mixtures [33]

System	Phase	Yield (%) ³⁸ Cl-for-Cl	³⁸ Cl-for-F
1.1-DCE	Cryst	13.1	
1.1-DCE - EtOH (6 : 4)	Cryst	11.3	
	Glassy	5.0	
	Liquid	2.8	
o-DCB	Cryst	11.2	
o-DCB - MeOH (1 : 9)	Cryst	11.2	
	Glassy	1.7	
	Liquid	1.9	
CCl ₄	Cryst	61.2	
CCl ₄ - C ₆ F ₆ (5 : 95)	Cryst	61.2	0.2
	Liquid	1.3	16.1

Here the yields are much lower and, in fact, resemble those obtained for liquid mixtures. Furthermore, in liquid mixtures of CCl₄ highly diluted with C₆F₆ the yield of the parent compound is low - according to dilution; that of labelling the other component is substantial. On the other hand in crystalline systems practically no labelling of the diluent can be found whereas the yield of parent product is the same as in the neat crystalline CCl₄.

In conclusion, considering once again the qualitative picture of radical recombinations, Fig. 6 shows a plot calculated by Noyes [4]. It demonstrates approximately the competition of a very efficient scavenger (with rate constant: $k_s \sim 10^{10} \text{ dm}^3/\text{mols}$) with different types of radical combination processes in a liquid. The three regions represent competition with (a) bulk radical reactions, (b) secondary and (c) primary geminate recombination. (Scavenger concentration is given in molarities, therefore -1 value represents 1 mol% and 1 represents 100 mol%, approximately.)

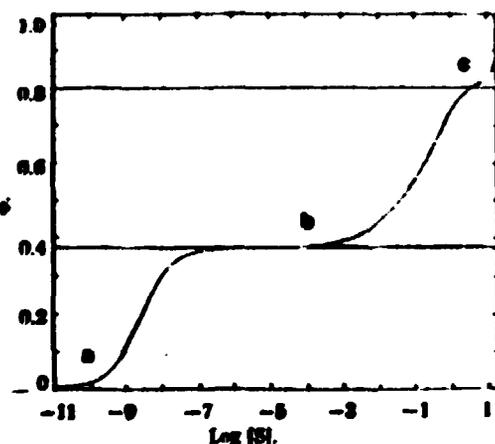


Fig. 6. Photochemical quantum yield dependence on concentration of very reactive scavenger [4]

Taking into account the experimental techniques presently used in hot atom studies, one gets the impression that the extent of primary recombinations can only be established by the density variation technique - combined with laborious total product yield analysis. And this can be applied to a very limited number of systems. We cannot, however, prevent or suppress this process by dilution technique unless we use systems which contain e.g. 99% of Br_2 as diluent.

On the other hand, the products of primary recombinations should not be different in any chemical aspect from those of the initial hot reactions: the time scale of 10^{-13} - 10^{-12} s and the lack of interactions with the surrounding molecules virtually does not allow any rearrangement of the original product.

Secondary geminate recombination is what we usually try to trace and suppress as the thermal process in the cage which superimposes the results of hot reactions. The role of this process can be established by using properly chosen reactive solvents in sufficiently high concentration. The work of Urch and coworkers [34,35] - continued recently also by Bhave and Rao [36,37] - concerning the relative reactivities of organic substances towards recoil Cl atoms in the liquid phase might give a guideline to how to choose such substances.

According to the plot in *Fig. 6* a very reactive scavenger (e.g. I_2 for Cl atoms) competes to some extent with secondary cage recombinations even if present in the concentration as low as usually applied in hot atom studies (0.5-2 mol%). This again calls our attention to the fact that to determine the extent of cage recombinations alone, radical combinations with the bulk substance have first to be established. Otherwise we observe the sum of these two processes. This aspect sometimes seems to be forgotten and different types of thermal reactions of recoil atoms are often lumped together.

The very slow progress of the field is justified by the complicated nature of recoil processes in condensed organic systems. That is all the more the reason for continuing investigations in this area with much greater intensity.

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