

# Photodecarbonylation of Dibenzyl Ketones and Trapping of Radical Intermediates by Copper(II) Chloride in Frozen Aqueous Solutions

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This paper presents a quantitative and qualitative study of the Norrish type I reaction of dibenzyl ketone (DBK) and 4-methyldibenzyl ketone (MeDBK), producing the benzyl radicals and consequently recombination products, in frozen aqueous solutions over a broad temperature range (−80 to 20 °C). This work extends previous research on the cage effects in various constrained media to provide information about the dynamics and reactivity of the photochemically generated intermediates at the grain boundaries of ice matrix. As the temperature of aqueous solutions decreases, the solute concentrations become high at layers covering ice crystals, causing efficient molecular segregation. The cage effect experiments have shown that diffusion of the benzyl radicals within such reaction aggregates is still remarkably efficient at temperatures below −50 °C, independently of the initial ketone concentration in the range of  $10^{-6}$ – $10^{-4}$  mol L<sup>−1</sup>. In addition, the study of trapping the benzyl radicals formed in situ by CuCl<sub>2</sub> was used as a qualitative probe of heterogeneous bimolecular reactions in the frozen aqueous matrix and on its surface. Molecules of both solutes were found to be segregated from the ice phase to the same location and underwent chemical reactions within diffusion and intermediates lifetimes limits. Understanding the fundamental physicochemical processes in ice is unquestionably important in related environmental or cosmochemical investigations.

## 1. Introduction

The Norrish type I reaction ( $\alpha$  cleavage) of ketones has been extensively studied in past decades.<sup>1</sup> The photolysis of dibenzyl ketone (DBK) in homogeneous solutions<sup>2–4</sup> (Scheme 1) results in the singlet excited state that intersystem crosses to the triplet state, which undergoes rapid primary  $\alpha$  cleavage in  $\sim 10^{-9}$  s following by slower decarbonylation ( $k \approx 10^7$  s<sup>−1</sup>).<sup>5–7</sup> Triplet radical pairs (<sup>3</sup>D and <sup>3</sup>D′) must intersystem cross to singlet radical pairs (<sup>1</sup>D and <sup>1</sup>D′) to yield 1,2-diphenylethane (DPE) and carbon monoxide (CO) or recombine back to starting material, or the radicals escape from the solvent cage. The quantum yields are usually high (e.g., 0.8 in benzene), and the small reaction inefficiency has been explained by cage recombination process.<sup>8</sup> In addition, the free benzyl radical undergoes the facile oxidation reaction ( $k \approx 10^6$  M<sup>−1</sup> s<sup>−1</sup>) in the presence of copper(II) chloride into benzyl chloride (BnCl).<sup>9</sup> In oxygen-saturated solutions, the benzyl radicals can also be trapped by oxygen to give peroxy radicals.<sup>10</sup>

The photodecarbonylation of nonsymmetrical 4-methyldibenzyl ketone (MeDBK) in homogeneous solutions provides three different 1,2-diphenylethane products: PhCH<sub>2</sub>CH<sub>2</sub>Ph, ArCH<sub>2</sub>CH<sub>2</sub>Ph, and ArCH<sub>2</sub>CH<sub>2</sub>Ar, where Ar = 4-methylphenyl, in a 1:2:1 statistical ratio (Scheme 2).<sup>4</sup> In contrast, a heterogeneous environment often causes a remarkable (cage) effect on the product mixture due to restricted translational diffusion of the radical intermediates.<sup>11,12</sup>

Hydrophobic organic material as well as ionic inorganic compounds are known to become spontaneously segregated at grain boundaries of the polycrystalline matrix at the phase transition when an aqueous solution is frozen.<sup>13,14</sup> The solute molecules are not incorporated into the solid ice, but they eventually ac-

cumulate in the layers surrounding the crystal walls, which solidify as temperature decreases.<sup>15–17</sup> Recent research results have provided sufficient evidence that organic compounds can undergo efficient light-induced chemical transformations in ice or snow.<sup>18–20</sup> While the laboratory experiments have shown that various environmentally important organic compounds experience unique photochemical transformations in ice,<sup>21–25</sup> it has also been revealed that snow-phase organic matter undergoes photolysis or photochemical oxidation under sunlight irradiation,<sup>20,26–30</sup> which could have large environmental consequences especially in polar regions where chromophoric organic pollutants are common trace constituents of natural ice and snow.

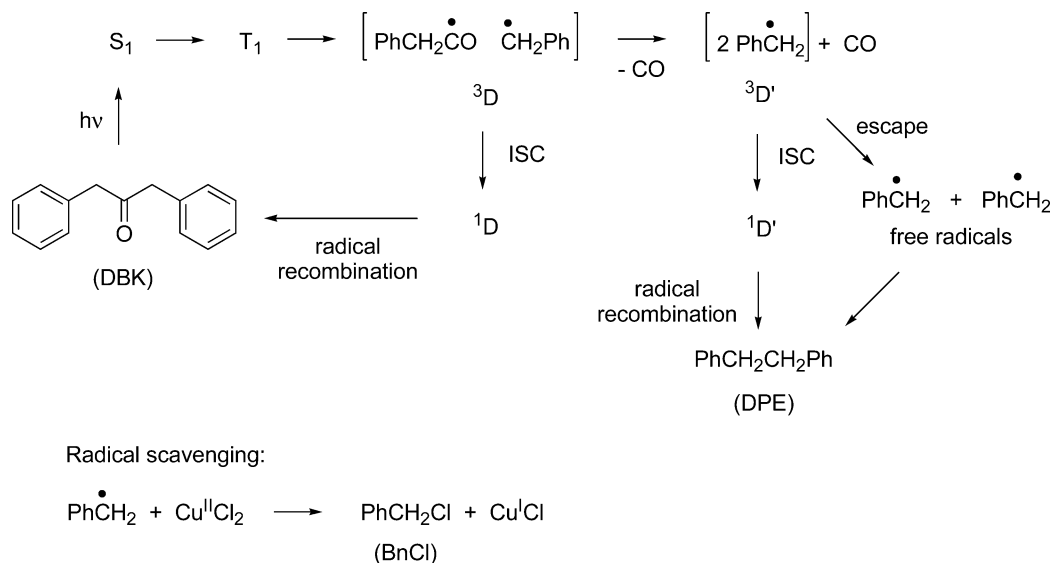
Photochemical reactions of substituted dibenzyl ketones have been reported to proceed in various organized media, such as cyclodextrins, Dianin's compound, zeolites, SiO<sub>2</sub> surfaces, liquid crystals, or micelles, in search of the cage effects, which can be defined as the fraction of radical pairs that undergo reactions within a primary reaction cage.<sup>11,31</sup> In this work, we extend this previous research by the study of DBK and MeDBK photochemistry in the matrix of frozen water over a broad temperature range (above −80 °C). Our results provide information on the dynamics and reactivity of the ketones and reaction intermediates at the grain boundaries of ice. The following study of trapping the benzyl radicals formed in situ by CuCl<sub>2</sub> is used as a qualitative probe of heterogeneous reactions in ice. In this connection, understanding the fundamental physicochemical processes in ice is important in related environmental,<sup>19</sup> cryogenic-water ice,<sup>32</sup> or cometary-ice<sup>33,34</sup> investigations.

## 2. Experimental Section

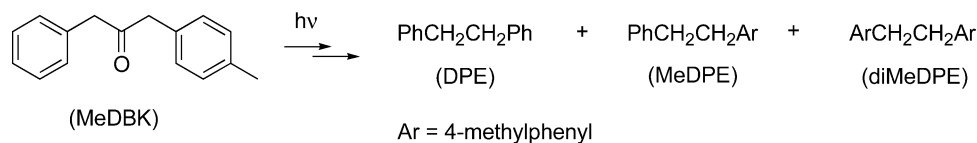
**Instrumentation.** Low-temperature experiments were accomplished in a cryostat MLW MK70. The solutions were centrifuged on an Eppendorf 5403 and homogenized in an

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## SCHEME 1



## SCHEME 2



ultrasound bath Tesla TESON 10. Gas chromatographs (FID), a Shimadzu GC-17A equipped with a J&W Scientific column (30 m, DP-5) and a Shimadzu GC-2010 equipped with a SPB-5 column (15 m, 5% diphenyldimethylsiloxane), were used for identification and quantification of the photoproducts. NMR spectra were recorded on a Bruker 300 MHz spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR data were measured in  $\text{CDCl}_3$  with tetramethylsilane as an internal standard. Mass spectra were recorded on a Fisons Instrument Trio 1000 spectrometer in positive mode with EI. Melting points were determined on a Kofler hot stage VEB Wägetechnik Rapido 79/2106. UV spectra were obtained on a Shimadzu UV-1601 instrument with matched 1.0-cm quartz cells.

**Chemicals.** Dibenzyl ketone (>99%) was obtained from Aldrich Chemical Co. and was used as received. Acetophenone (>99%), copper(II) chloride dihydrate (p.a.), and  $\text{Na}_2\text{SO}_4$  (p.a.) were purchased from Lachema Co. and were used as received. 1,2-Diphenylethan (>98%, Chemapol Co.) and *n*-hexadecane (p.a., Schuchardt; an internal standard for the GC measurements) were used as received. Dichloromethane (p.a.) was purchased from Penta Co. and was purified by distillation through a vacuum-sealed column (70 cm) packed with glass beads. Water was purified by the reverse osmosis process on an Aqua Osmotic 03, and its quality complied with U.S. Pharmacopeial Standards (USP). The synthesis of the starting compounds and photoproducts, 4-methyldibenzyl ketone (MeDBK), 4,4'-dimethyldibenzyl ketone (diMeDBK), 1-methyl-4-phenethylbenzene (MeDPE), and 1,2-dimethyl-4-phenethylbenzene (diMeDPE), is described in the Supporting Information.

**Irradiation Procedures.** *4-Methyldibenzyl Ketone (MeDBK) Photochemistry.* Aqueous ketone solutions were prepared by sonication of the saturated solutions ( $c \sim 2.0 \times 10^{-4} \text{ mol L}^{-1}$ ), followed by dilution with water to a desirable concentration. Oxygen, an efficient triplet state quencher, was removed from the samples by bubbling the solutions with argon for 15 min. The aqueous solutions (10 mL) in Pyrex tubes (transparent at  $\lambda > 280 \text{ nm}$ ), sealed with septa and placed in the merry-go-round

apparatus, were solidified in an ethanolic bath of the cryostat. In all low-temperature experiments, the samples were kept in the bath at  $-20^\circ\text{C}$  for 30 min and the temperature was then adjusted as necessary. The samples were irradiated using a 125-W medium-pressure mercury lamp (Tselamp Co., Praha, Czech Republic). Solutions were extracted with dichloromethane solution of hexadecane (2 mL), used as an internal standard. Identification and quantification of the photoproducts was carried out by the GC and GC-MS analyses by comparison with the authentic compounds. The relative standard deviation for triplicate samples was found below 8% in all analyses. The samples with a low concentration ( $10^{-6} \text{ mol L}^{-1}$ ) were simultaneously irradiated in 24 Pyrex tubes (15 mL each), and the collected melted liquid (360 mL) was extracted with dichloromethane solution of hexadecane (15 mL). The dichloromethane sample was concentrated in vacuo to 1 mL and analyzed as above.

*Photolysis of DBK/diMeDBK Mixtures.* Aqueous solutions of both ketones were prepared separately and mixed together in a ratio corresponding to approximately equimolar concentration. The irradiation procedure and analyses were performed as above.

*Irradiation of DBK in the Presence of  $\text{CuCl}_2$ .* Aqueous dibenzyl ketone solutions were prepared by sonication and centrifugation of the saturated solutions ( $c \approx 2.0 \times 10^{-4} \text{ mol L}^{-1}$ ) for 15 min at  $4^\circ\text{C}$ , followed by dilution with water to a desirable concentration. The irradiation and analysis procedures were the same as those with MeDBK samples; only the corresponding amount of  $\text{CuCl}_2$  was dissolved in the samples prior to bubbling the solution with argon. Because the concentration of DBK could not be increased due to a limited solubility in water, *tert*-butyl alcohol was added to extend the experimental possibilities in several experiments.

*Ice Surface Photolysis Experiments.* Aqueous  $\text{CuCl}_2$  solutions (ca. 15 mL) were sputtered on a cold ( $-20^\circ\text{C}$ ) quartz finger ( $15 \times 5 \text{ cm}$ ) to form a uniform layer of approximately 5-mm thickness. The finger, temporarily filled with liquid nitrogen,

**TABLE 1: Temperature Dependence of the Cage Effect in the Photolysis of MeDBK<sup>a</sup>**

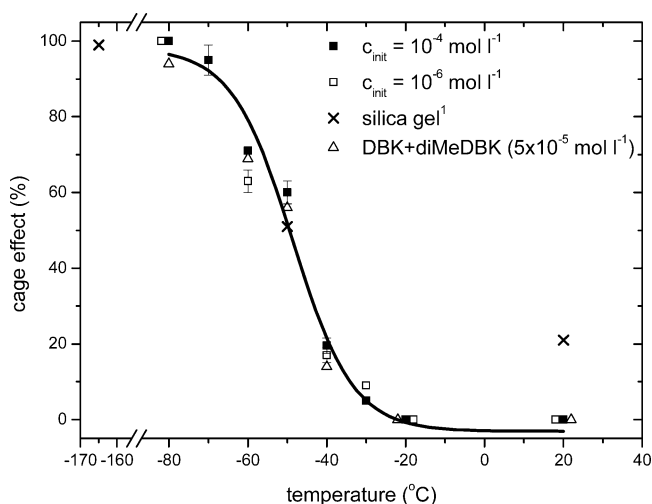
temp (°C)	initial concentration (mol L <sup>-1</sup> )	conversion (%)	cage effect 1 (%)	cage effect 2 <sup>c</sup> (%)
20	1.4 × 10 <sup>-4</sup>	17	~0 <sup>b</sup>	~0
	1.4 × 10 <sup>-4</sup>	46	~0	
	1.0 × 10 <sup>-6</sup>	56	~0	
-20	1.8 × 10 <sup>-4</sup>	7	~0	
	1.8 × 10 <sup>-4</sup>	16	~0	
	1.8 × 10 <sup>-4</sup>	21	~0	
-30	1.0 × 10 <sup>-6</sup>	56	~0	
	1.8 × 10 <sup>-4</sup>	10	~0	~0
	1.8 × 10 <sup>-4</sup>	30	~0	
	1.8 × 10 <sup>-4</sup>	81	~0	
	0.5 × 10 <sup>-4</sup>	37	~0	
-40	0.2 × 10 <sup>-4</sup>	96	~0	
	1.0 × 10 <sup>-6</sup>	52	9.0	
	1.5 × 10 <sup>-4</sup>	12	17.5	13.5
	1.5 × 10 <sup>-4</sup>	20	18.5	
	0.5 × 10 <sup>-4</sup>	42	23.5	
-50	1.0 × 10 <sup>-6</sup>	47	17.0	
	1.7 × 10 <sup>-4</sup>	36	59.5	55.6
	1.7 × 10 <sup>-4</sup>	48	58.4	
-60	0.6 × 10 <sup>-4</sup>	58	61.5	
	1.4 × 10 <sup>-4</sup>	20	72.0	69.2
	1.4 × 10 <sup>-4</sup>	36	72.0	
	0.5 × 10 <sup>-4</sup>	32	70.5	
-70	1.0 × 10 <sup>-6</sup>	38	62.6	
	1.5 × 10 <sup>-4</sup>	46	92.0	
	0.3 × 10 <sup>-4</sup>	72	>99	
-80	1.6 × 10 <sup>-4</sup>	6	>99	94.5
	1.6 × 10 <sup>-4</sup>	20	>99	
	1.0 × 10 <sup>-6</sup>	16	>99	

<sup>a</sup> The reproducibility of the measurements was ±8%. <sup>b</sup> This value corresponds to a 1:2:1 statistical product ratio. <sup>c</sup> The cage effect based on the photochemistry of the DBK + diMeDBK mixture ( $c_{\text{ketone}} = 5 \times 10^{-5} \text{ mol L}^{-1}$ ).

was immersed into the quartz reactor (sleeve) containing pure solid DBK (ca. 15 mg) at the bottom under argon atmosphere. The crystals were gradually heated by a hot-water bath to evaporate, while the gaseous compound condensed at the cold ice layer under lower pressure (2–4 Torr). The layer was then irradiated using a 125-W medium-pressure mercury lamp through a Pyrex glass wall (transparent at  $\lambda > 280 \text{ nm}$ ) in a cryostat box and the corresponding temperature of the layer was adjusted by ethanol as a cooling medium inside the finger. Finally, the ice matrix was removed from the finger and divided into two or three parts, melted, and extracted with dichloromethane. The product distribution was analyzed via GC and GC–MS as described above.

### 3. Results and Discussion

**3.1. Photodecarbonylation of MeDBK.** The steady-state irradiation of the MeDBK or DBK/diMeDBK aqueous solutions in sealed Pyrex tubes ( $\lambda > 280 \text{ nm}$ ) provided photoproducts DPE, MeDPE, and diMeDPE in a concentration ratio, which was strongly dependent on ambient temperature. No other photoproducts were detected at lower conversions; however, the exhausted photolysis (>50% conversions) caused the formation of a small amount of nonidentified byproducts as was also observed elsewhere.<sup>35</sup> All samples were cooled slowly at –20 °C for 30 min (the solutions were visually frozen) to guarantee the comparable initial conditions; then the cooling bath temperature was adjusted accordingly. Table 1 shows the variation on the cage effect as a function of temperature and MeDBK conversions for two different initial concentrations,  $c_{\text{MeDBK}} = 10^{-4}$  and  $10^{-6} \text{ mol L}^{-1}$ . The cage effect of the solid ice medium



**Figure 1.** Temperature dependence of the cage effect in the photolysis of MeDBK samples or DBK/diMeDBK mixtures. The conversions varied between 6% and 96%. Each point is an average at least of three measurements, and the error bars represent the standard deviation.<sup>1</sup> Data from photolysis of 4-methoxy-4'-methyl-DBK on silica gel surface are from ref 36. A Boltzmann sigmoidal curve is shown for MeDBK (■, □) only.

has been expressed similarly to that used in the studies of micellar systems:<sup>31</sup>

$$\text{cage effect 1} = \frac{[\text{MeDPE}] - ([\text{DPE}] + [\text{diMeDPE}])}{[\text{DPE}] + [\text{MeDPE}] + [\text{diMeDPE}]} \times 100 (\%)$$

(MeDBK photolysis)

$$\text{cage effect 2} = \frac{([\text{DPE}] + [\text{diMeDPE}]) - [\text{MeDPE}]}{[\text{DPE}] + [\text{MeDPE}] + [\text{diMeDPE}]} \times 100 (\%)$$

(DBK–diMeDBK mixture photolysis)

where the product concentrations are in moles. While the conversion had no significant effect on the ratio in the study range (6–96%), the temperature exhibited a strong influence on the cage effect values. A statistical 1:2:1 ratio of the products in liquid solutions and samples kept above –20 °C is well in contrast with results obtained at low temperatures. The cage effect increased consistently with decreasing temperature, and eventually leveled off to 100% below –70 °C. The data points in Figure 1, showing the cage effect dependence on temperature, were closely fitted with a Boltzmann sigmoidal curve, which allowed us to estimate the inflection point at approximately –50 °C. The initial concentrations in the interval of  $10^{-4}$  and  $10^{-6} \text{ mol L}^{-1}$  had practically no effect on the shape of the curve.

For this study, the cage effect describes the probability of the recombination of the geminate benzyl radical pair within an aggregate, which is formed at the grain boundaries or interstitial pores of polycrystalline ice. Because all experiments with the DBK/diMeDBK mixtures revealed that cross radical coupling is feasible at least to some extent, the parent compounds had to be aggregated prior the photolysis started. Keeping the samples in the frozen state after the irradiation for hours or days did not change the photoproduct concentrations. The equilibrium (slow) freezing at –20 °C guaranteed the same rate of the initial segregation process from the ice phase. It is well known that when liquid aqueous solutions start to solidify, a liquid or quasi-liquid layer covers the surface of ice crystals and it is composed of highly concentrated solution of the solute

molecules ejected from newly formed crystalline phase.<sup>16,17,37,38</sup> Thus, organic molecules aggregate as self-organized clusters of hydrophobic molecules surrounded by water molecules. As the temperature further drops, migrations and conformational motions are suppressed,<sup>24,39</sup> and water molecules are further removed from the clusters, making the average intermolecular distances among the solutes shorter. At the same time, a lower temperature as well as a more rigid environment should put severe restrictions on the diffusion. The observation of an increasing cage effect at low temperatures supports the latter concept. The inflection point at  $-50\text{ }^{\circ}\text{C}$  measured corresponds to a state, in which the rate constant of radical escape from the cluster equals that of the recombination process within the primary cage. The rate constant of decarbonylation is known to be close to  $10^7\text{ s}^{-1}$  (at  $20\text{ }^{\circ}\text{C}$ ).<sup>5-7</sup> While the recombination of two radicals is practically immediate if the radical pair has the singlet multiplicity, the escape from the reaction site is endorsed by the triplet multiplicity.<sup>8,35,40</sup> Because the radicals were initially formed in a close proximity, only relatively unconstrained diffusion may guarantee that the cage effect is absent. Some restrictions were observed already at  $-30\text{ }^{\circ}\text{C}$  (0–9%), at which water molecules are known to not participate in certain chemical (solvolytic) reactions as nucleophiles, such as a photosolvolysis of halogenated aromatic compounds.<sup>22-24</sup> While hydrogen bonding or hydrophobic forces are expected to control extensively the intermolecular reactions, they do not prevent the benzyl radicals to migrate. Such a motion is still apparent at  $-60\text{ }^{\circ}\text{C}$ , as proved by the cage effect value of  $\sim 70\%$ .

This study parallels the cage effects studies employing the Norrish type I reactions of dibenzyl ketones, benzyl esters, or sulfones on silica gel by de Mayo,<sup>36,41</sup> Turro,<sup>35,42,43</sup> and their co-workers, or on polyethylene films by Weiss and co-workers.<sup>44</sup> Silica gel surfaces have the silanol and siloxane polar functional groups,<sup>45</sup> and the most important interactions of the substrate with the surface are hydrogen bonding and dipole–dipole interactions, similar to those of ice crystal surface. Silica gel solid surface was shown to restrict the diffusion of the geminate radical pairs already at  $20\text{ }^{\circ}\text{C}$ ,<sup>36</sup> and the cage effect substantially increased with decreasing temperature as was also observed in the ice matrix in this work (Figure 1). The coverage (i.e., ketone surface concentration) of silica gel and the water content had only modest and insignificant effects, respectively.<sup>41</sup> The preexponential factors and activation energies of decarbonylation of phenylacetyl radicals in homogeneous solutions were reported.<sup>46</sup> The rate constant of this process was found to drop approximately 1 order of magnitude with a temperature decrease of  $50\text{ }^{\circ}\text{C}$  due to the contribution of specific and nonspecific solvations. This is certainly relevant for this study, but heterogeneity of frozen aqueous solutions must be considered. One-half of the benzyl radicals are formed about 2 orders of magnitude faster than those produced by a slower decarbonylation; thus two kinetic processes coexist. When temperature drops, the rate constants of both processes decrease at the same time as that of diffusion in a still more rigid ice environment. Interestingly, the same cage effect value ( $\sim 50\%$ ) was obtained on silica gel and in ice at the inflection point of  $-50\text{ }^{\circ}\text{C}$  (Figure 1), showing that the translation dynamics of the radicals is comparable in both matrixes once the aqueous samples are solidified. While an increase of the cage effect values at lower temperatures is in accord with slower diffusion, the effect of temperature on the decarbonylation rate constants is not easily quantified. A longer phenylacetyl radical lifetime should enhance the efficiency of the recombination of  $^3\text{D}$  via  $^1\text{D}$  to the starting ketone (Scheme 1), which is supported by lower quantum

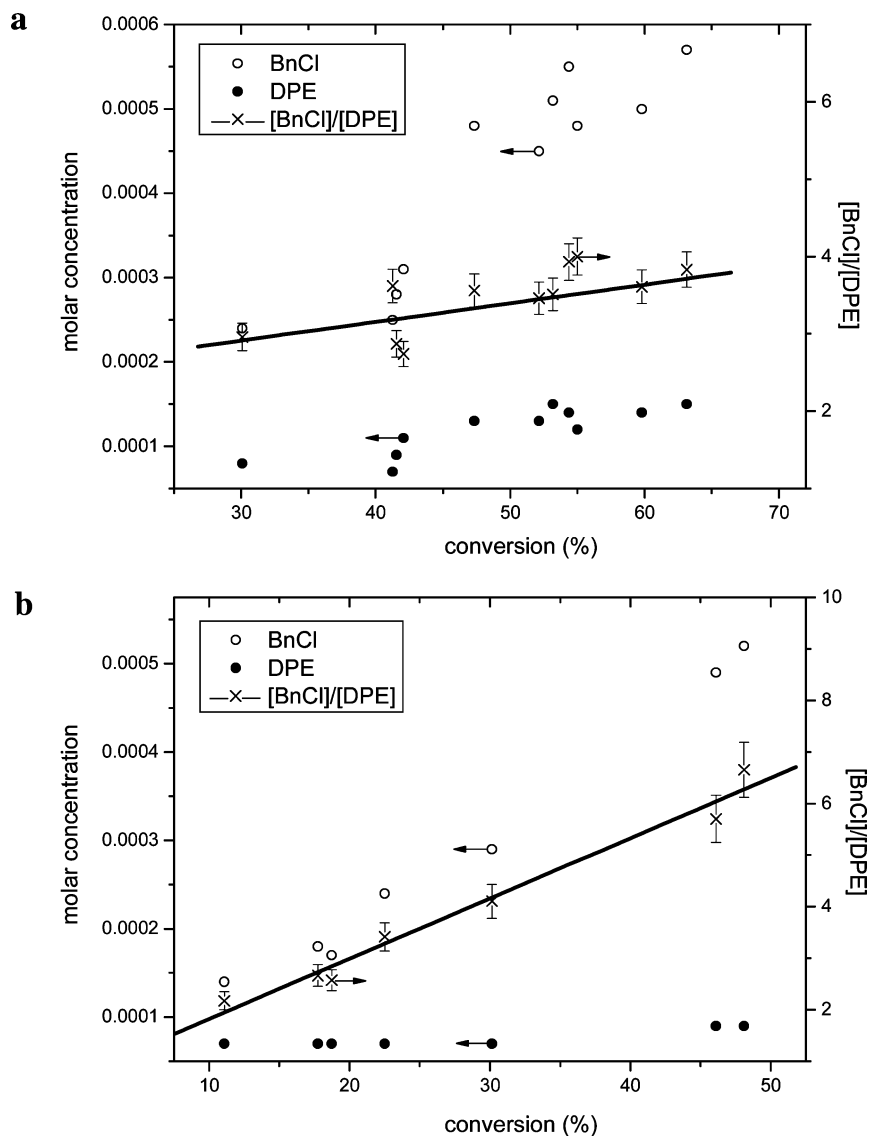
efficiencies measured at low temperatures, or it should raise the probability for the radical to escape from the reaction site when the production of DPE is not immediately accessible. The nature of the dependence measured in ice cannot be easily extrapolated from data in homogeneous media or micelles;<sup>31,36,47</sup> even comparison of the cage effects in liquid or semi-liquid and frozen matrixes is difficult. Due to similarities of the data obtained with ice and silica gel surfaces, we can conclude that diffusion in ice is still remarkably efficient at relatively low temperatures and that the starting ketone in ice is not incorporated into its crystal structure. Aggregated ketones must be microscopically dispersed<sup>48</sup> on the ice crystal surfaces, but a uniform coverage can be hardly achieved. Because the initial ketone concentrations within 2 orders of magnitude were found to have negligible effects on the inflection curves, aggregates must be large enough to exhibit such consistent statistical data.

**3.2. Photodecarbonylation of DBK in the Presence of  $\text{CuCl}_2$ .** Chemical reactions between hydrophobic organic molecules and inorganic salts in the ice matrix have not been studied in detail; yet the production of some reactive species, such as  $\text{HO}\cdot$ ,  $\text{NO}_x$ , or halogen atoms in the snowpack or ice, is well established, and their possible reactions with organic precursors are proposed.<sup>20</sup> The present study of photochemistry of a highly hydrophobic DBK in the presence of water-soluble  $\text{CuCl}_2$  in the ice matrix was aimed to establish whether both solute molecules can be segregated from the ice phase to the same location where they undergo chemical reactions. There were several variables that affected the course of the reaction of this two-component system, such as conversion, stoichiometry, temperature, and the phase changes. The concentration ratio  $[\text{BnCl}]/[\text{DPE}]$  of the two exclusive photoproducts, benzyl chloride (BnCl) and 1,2-diphenylethane (DPE) (Scheme 1), was followed. Because  $\text{CuCl}_2$  absorbs UV radiation in the region of interest, the samples with the same chloride concentrations were used in the quantum efficiency measurements or the values were corrected.

**Conversion.** The formation of both products, BnCl and DPE, upon irradiation at  $\lambda > 280\text{ nm}$  was observed in samples frozen from the mixed aqueous solutions at  $-20\text{ }^{\circ}\text{C}$ ; this temperature guaranteed that the samples were visually completely solidified.<sup>24</sup> Figure 2a,b (each point in the graph represents an independent sample photolyzed) shows that the dependencies of the concentration ratios  $[\text{BnCl}]/[\text{DPE}]$  on conversion were linear for both  $\text{CuCl}_2$  concentrations (two benzyl radicals are necessary to form DPE, while only one is sufficient for BnCl production). The slope corresponding to a lower concentration ((a),  $c_{\text{CuCl}_2} = 5 \times 10^{-3}\text{ mol L}^{-1}$ ) was almost 4 times lower than that of the more concentrated samples ((b),  $c_{\text{CuCl}_2} = 2 \times 10^{-2}\text{ mol L}^{-1}$ ), which is simply proportional to the ratio of the initial chloride concentrations. The relative rates of BnCl formation as compared to that of DPE were higher for two different  $\text{CuCl}_2$  concentrations by factors of 3.9 and 7.8, respectively (thus, only in a  $\sim 1:2$  ratio). A satisfactory linearity of all dependencies, and an ability of the reaction system to reach high conversions, suggested the existence of an equilibrated reaction mixture but a specific access of the radicals to the trapping agent to some extent. The fact that the product ratio is not constant in the course of the photolysis is an emergent characteristic of the system, and it had to be considered in the subsequent experiments.

Linear conversion dependencies indicate that the probability of the photoreaction among DBK and  $\text{CuCl}_2$  molecules was unaffected in the course of the reaction. Increasing the copper chloride concentration only raises the probability that the benzyl





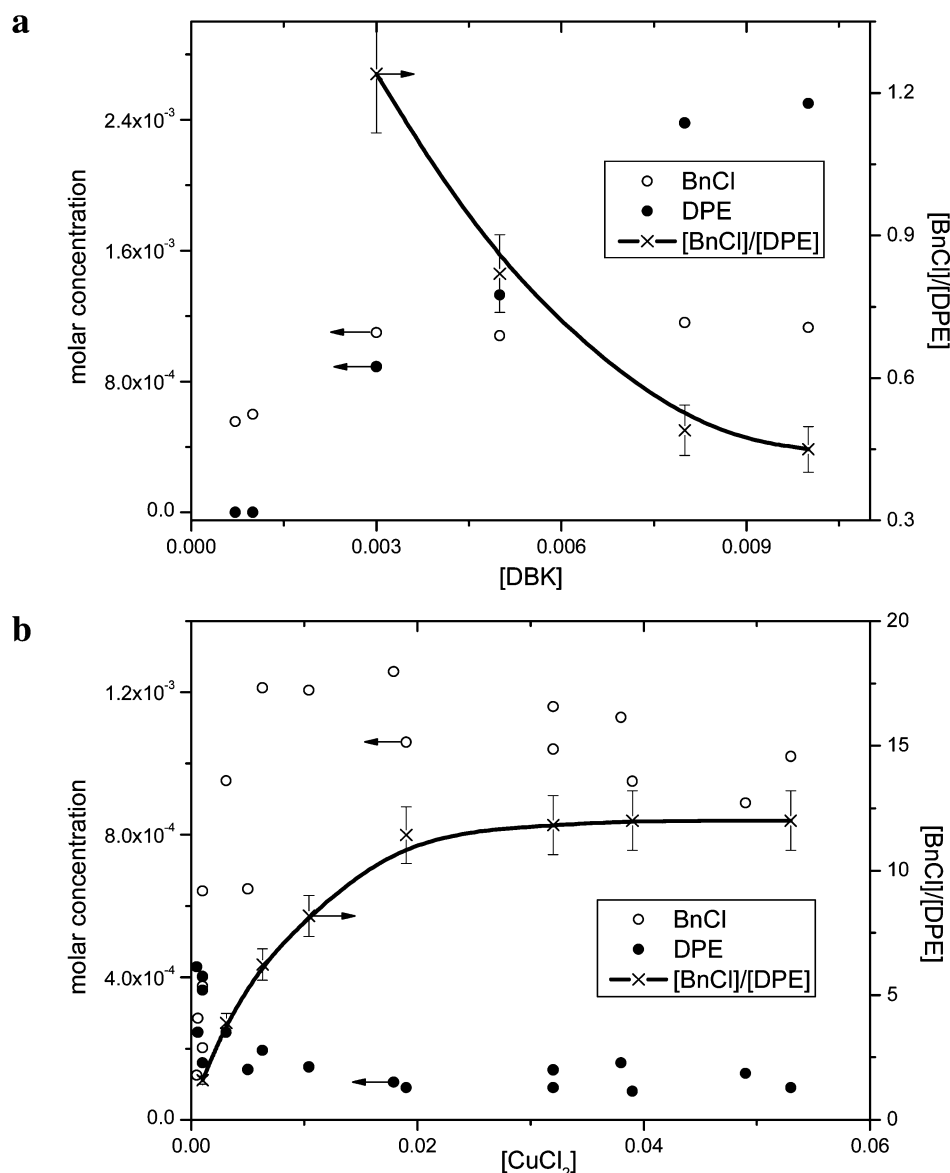
**Figure 2.** The conversion-dependent photochemistry of DBK ( $c_{\text{DBK}} = 1.5 \times 10^{-3}$ ) in the presence of  $\text{CuCl}_2$  ( $c_{\text{CuCl}_2} =$  (a)  $5 \times 10^{-3}$ , (b)  $2 \times 10^{-2}$  mol  $\text{L}^{-1}$ ) in ice at  $-20^\circ\text{C}$ . Each point is an average at least of three measurements, and the error bars represent the standard deviation.

radical will be oxidized, but, at the same time,  $\text{CuCl}_2$  is a strong UV absorber that lowers the observed photochemical efficiencies in the mixture. As a result, photolysis of DBK in the  $\text{CuCl}_2$  clusters, with a high probability of BnCl formation, must be photochemically less efficient than that of DBK residing outside the cluster. If the benzyl radicals formed are not directly adjacent to copper chloride, diffusion, still largely available at this temperature as shown in the preceding paragraph, would control the reaction efficiency and partitioning between the two products. The photolysis of homogeneous liquid aqueous solutions provided constant  $[\text{BnCl}]/[\text{DPE}]$  values practically independent of the conversion in the range of 5–90% ( $\sim 0.8$  and  $\sim 1.5$  for  $c_{\text{CuCl}_2} = 5 \times 10^{-3}$  and  $2 \times 10^{-2}$  mol  $\text{L}^{-1}$ , respectively); that is, a  $\sim 3$ -fold increase in the BnCl formation efficiency was observed in ice as compared to liquid water. We believe that heterogeneity of frozen solutions itself and complex kinetics are responsible for such a specific behavior. Additionally, the fact that both solutes were found to be localized within the diffusion limits of the reaction implies that the exclusion force from the ice phase does not reveal any significant selectivity despite different physical properties of both compounds.

**Relative Stoichiometry.** The relative stoichiometry is one of the most important variables in any self-assembly and

aggregation study. Based on the previous results, the aggregates and the ice cage should allow efficient rotational and translational motion of small organic molecules at relatively low temperatures. Figure 3 presents the product concentrations and the  $[\text{BnCl}]/[\text{DPE}]$  ratio in cases that one of the initial starting-compound concentrations is a variable. Both dependencies leveled off at the corresponding reactant concentrations, at which any further addition had no effect on the product ratio. The samples with various  $\text{CuCl}_2$  concentrations had to be irradiated over different periods of time to reach desirable (equal) conversions because the salt acts as an internal optical filter affecting the observed reaction efficiency. The concentration limits advocate the idea of access related processes at the grain boundaries; that is, excess molecules may be too distant to be reached by diffusion.

**Temperature.** Temperature plays the most important role when bimolecular reactions at the phase transition are considered. While the product concentration ratio  $[\text{BnCl}]/[\text{DPE}]$  was identical in the temperature interval of  $-5$  to  $20^\circ\text{C}$ , it raised with decreasing temperature linearly for both  $\text{CuCl}_2$  concentrations selected (Figure 4) with slopes proportional to the ratio of the initial chloride concentrations. It is apparent from the graphs that the absolute DPE concentration only slightly

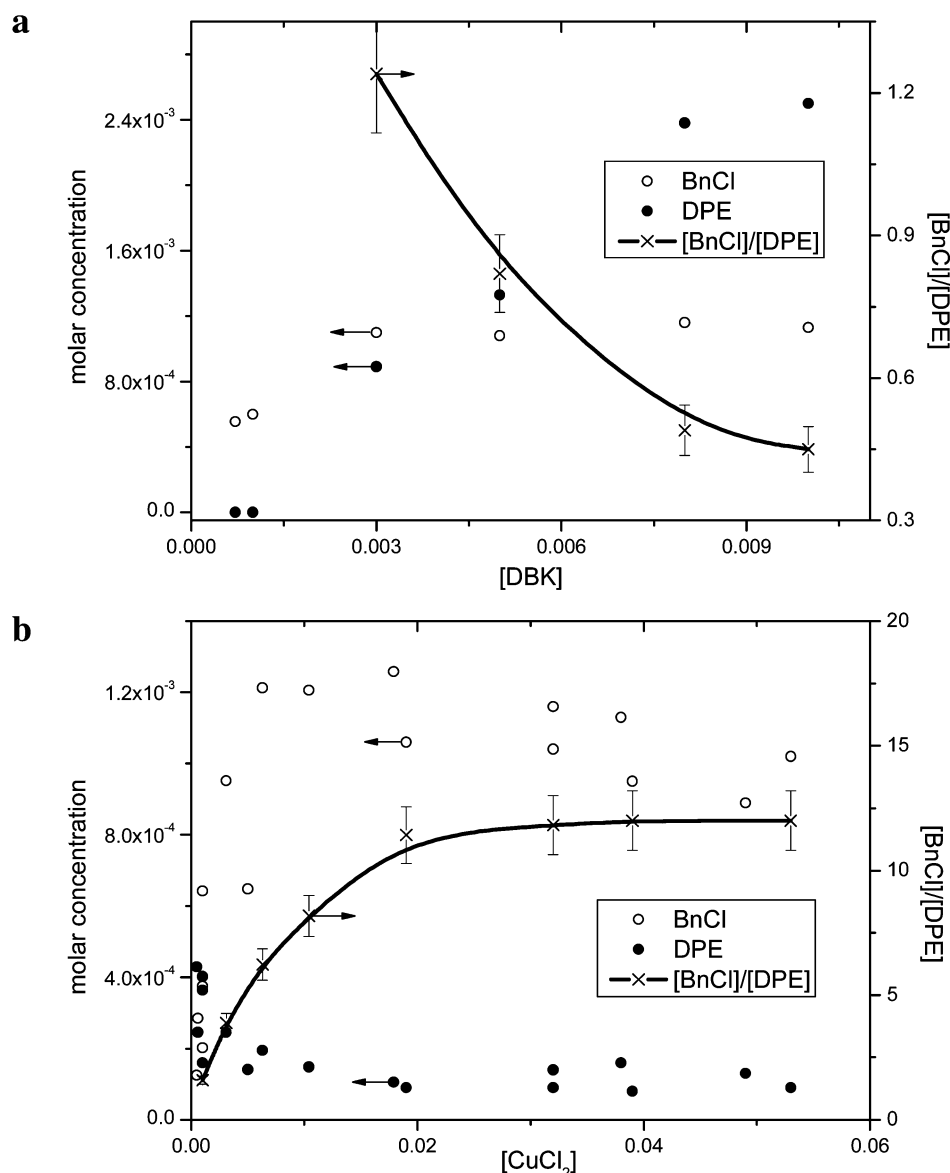


**Figure 3.** The photolysis of DBK in the presence of CuCl<sub>2</sub> at -20 °C: (a)  $c_{\text{CuCl}_2} = 1 \times 10^{-2} \text{ mol L}^{-1}$ ,  $c_{\text{DBK}}$  is a variable; (b)  $c_{\text{DBK}} = 2.5 \times 10^{-3} \text{ mol L}^{-1}$ ,  $c_{\text{CuCl}_2}$  is a variable. The conversions were kept between 30% and 50%, and the absolute concentrations were corrected on the results shown in Figure 2. Each point is an average at least of three measurements, and the error bars represent the standard deviation.

decreased with decreasing temperature, while that of BnCl considerably increased and eventually leveled off.

Recent studies made it possible to quantify the partitioning of salts between the solid and solution phase in ice, for example, by NMR,<sup>17,49,50</sup> and, at the same time, there is a strong evidence that heterogeneous reactions of gases with halides in liquid or quasi-liquid layers are the source of halogen radicals in nature.<sup>51–54</sup> Several authors have showed that “quasi-brine layer” (QBL), the unfrozen NaCl solution phase on ice crystals, exists at temperatures below the eutectic point.<sup>17,53,54</sup> Similarly, both CuCl<sub>2</sub> and DBK undoubtedly coexist in brine or QBL at temperatures above -20 °C, in which hindered but equilibrated diffusion is allowed. Oxidation of the benzyl radicals prevailed at lower temperature; thus the local concentrations increased by lowering the temperature, making the bimolecular reactions more feasible. Temperature does affect unimolecular reactions of DBK as mentioned before, but the effect should not be significant in this temperature range. It seems also possible that CuCl<sub>2</sub> may partially crystallize at the grain boundaries, which should not, however, prevent the photoreaction of the benzyl radicals on the crystal surface.

**Surface Photochemistry.** To test the ability of CuCl<sub>2</sub>, being excluded from the frozen ice phase, to oxidize the benzyl radicals produced from DBK condensed on the ice surface from the gas phase, the coldfinger experiments were performed. A CuCl<sub>2</sub> aqueous solution was sprayed at a cold quartz finger to produce a 5-mm thick layer of ice, on which DBK was later deposited by condensation processes under reduced pressure. It was found that the photochemical formation of both products, BnCl and DPE, largely depended on the initial chloride concentration (Table 2). While no oxidation of the benzyl radicals was observed at relatively low concentrations, a significant portion of BnCl was produced at  $c_{\text{CuCl}_2} > 0.1 \text{ mol L}^{-1}$ . Copper dichloride is partially rejected during the freezing toward the ice surface, which makes it available to the reactions not only with gaseous reactants but also with condensed organic matter. An efficient oxidation also proceeded on the surface of pure copper chloride crystals at the same temperature; thus reactions on the surface of locally crystallized salt at the grain boundaries should be considered. The mass balance was relatively low in all analyses (<50%) because a large fraction of deposited DBK volatilized off the surface during the experiment. This study



**Figure 4.** The temperature-dependent photolysis of DBK ( $c_{\text{init}} = 2 \times 10^{-3} \text{ mol L}^{-1}$ ) in the presence of  $\text{CuCl}_2$ . The conversions were kept between 40% and 60%, and the absolute concentrations were corrected on the results shown in Figure 2. Each point is an average at least of three measurements, and the error bars represent the standard deviation.

**TABLE 2: Ice Surface Photochemistry at  $-20^\circ\text{C}$**

$\text{CuCl}_2$ concentration ( $\text{mol L}^{-1}$ )	conversion (%)	BnCl/DPE ratio <sup>a</sup>
$2.0 \times 10^{-3}$	51	DPE only
$2.0 \times 10^{-3}$	94	DPE only
$5.0 \times 10^{-3}$	15	DPE only
$2.0 \times 10^{-2}$	86	DPE only
$1.0 \times 10^{-1}$	4	$\sim 0.02$
$3.0 \times 10^{-1}$	32	$\sim 0.18$
$5.0 \times 10^{-1}$	8	$\sim 0.71$
$\text{CuCl}_2 \cdot \text{H}_2\text{O}^b$	12	100

<sup>a</sup> The mass balance was low ( $<50\%$ ) due to the loss by evaporation.

<sup>b</sup> A crystalline pure solid.

served to prove that a portion of the ejected material from the ice matrix could have a direct contact with a vapor-condensed material on the surface of ice, thus making the corresponding heterogeneous chemical reactions possible.

#### 4. Conclusion

Despite the variety of studies describing physical aspects of the processes at the grain boundaries of ice or snow,<sup>38</sup> relatively

few deal with chemical changes. We recently demonstrated that photochemistry of organic compounds is remarkably efficient and that both intra- and intermolecular reactions are feasible in the ice matrix.<sup>21,23,24,39</sup> In this paper, the study of the partitioning between uni- and bimolecular reactions of nonsymmetrical dibenzyl ketone helped to understand the diffusion dynamics of small molecular fragments in a wide temperature range. It was found that the behavior of the ketones aggregated in clusters at the ice grain boundaries is similar to that of silica gel surfaces and that diffusion is still relatively efficient below  $-50^\circ\text{C}$ . Given the strength and directionality of the freezing process, it was further questionable whether bimolecular reactions can occur among hydrophobic and hydrophilic compounds in the layer covering the crystalline ice surfaces at the grain boundaries. In this connection, photochemistry of mixed frozen solutions of DBK and  $\text{CuCl}_2$  served as a model system, in which inorganic salt undergoes a chemical reaction with organic molecules at moderate temperatures (above  $-20^\circ\text{C}$ ), and it was found that the reactions are feasible in the bulk as well as on the ice surface. The concentration effect during freezing of aqueous solutions, known since the 1960s in connection with the acceleration of

some thermal chemical reactions,<sup>15,55–59</sup> was found as the most important force influencing bimolecular photochemical reactions, and it must play an important role in natural ice environments where chromophoric organic pollutants are common trace constituents.<sup>60–62</sup>

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**Supporting Information Available:** Synthesis details for starting compounds and photoproducts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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