The Radical Cation of Methylcyclohexane

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It is shown by pulse radiolysis that the transient absorption in N₂O-saturated or CO₂-saturated methylcyclohexane (MCH), peaking at about 570 nm, is due to the solvent radical cation MCH⁺. From simulations with the semiempirical $t^{-0.6}$ rate law, it is concluded that MCH⁺ is of very high mobility: at 133 K (supercooled liquid) $D_{exp} = (1.06 \pm 0.2) \times 10^{-6}$ cm² s⁻¹, which is ca. 400 times faster than expected from diffusion. At room temperature MCH⁺ is about 11 times faster than diffusion, and this is in perfect agreement with the conductivity of MCH⁺, as measured by Warman et al. For the high mobility of MCH⁺ an activation energy of 8.9 ± 0.3 kJ/mol is found. The rate constant for scavenging MCH⁺ with norbornadiene (NBD) is $k_2(133 \text{ K}) = (1.8 \pm 0.5) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. This is again 80 times faster than the diffusional rate constant. From the intercepts of the semiempirical $t^{-0.6}$ linearity plots, the free ion spectra were derived. The free ion absorbance at 133 K turns out to be 2.0 times smaller than that at room temperature. The free ion yield at low temperatures therefore was derived to be $G_{fi}(127-153 \text{ K}) = 0.06 \pm 0.015 (100 \text{ eV})^{-1}$. From the free ion intercept at room temperature the absorption coefficient ϵ was determined: $\epsilon_{570nm}(MCH^+) \ge 2300 \text{ M}^{-1} \text{ cm}^{-1}$. Without the electron scavengers N₂O or CO₂ the olefinic cation methylcyclohexene⁺ is found to replace MCH⁺. This indicates that some excited species, usually quenched by N₂O or CO₂, is the precursor of the high-mobility radical cation MCH⁺.

Introduction

In pulse radiolysis of a N₂O-saturated solution in methylcyclohexane (MCH) a transient absorption in the visible wavelength range, peaking at 570 nm, is observed at low temperatures. We have briefly reported about the characteristics of this band in a preliminary report,¹ particularly about the abnormally high mobility of that transient. We tentatively assigned it to the radical cation MCH⁺ of the solvent. Previously Mehnert et al.² reported a 500 nm band at room temperature with equal assignment. Over the past years, arguments were given that the high mobility should be assigned to the proton transfer mechanism.³ The aim of the present paper is to give proof for the assignment of the 570 nm band to the radical cation MCH⁺ and that its high mobility must correspond to a fast chargetransfer process through the solvent MCH.

For this purpose, most experiments were performed with liquid samples at low temperatures between ca. -90 and -146 °C (127–183 K), to slow down the geminate ion kinetics and to observe a higher yield (time resolution ca. 50 ns). Additional experiments were done at room temperature with the pulse radiolysis equipment at Tokai-mura, University of Tokyo (time resolution ca. 1 ns). The most important arguments are derived from simulations of the geminate ion recombination kinetics with the semiempirical $t^{-0.6}$ rate law by van den Ende et al.,⁴ which predicts the linearity of the geminate ion absorption with $t^{-0.6}$.

Experimental Section

Pulse Radiolysis. The technique of pulse radiolysis with a Febetron 705 (Hewlett Packard) accelerator for 30 ns pulses of 2 MeV electrons has been used as previously reported.^{5,6} All

experiments were performed at low temperatures, typically in the range from -90 to -146 °C in the liquid state (for T < -127 °C in a supercooled liquid state). The stainless steel cell had an optical path length of 2 cm. A typical dose was between 50 and 150 Gy. Dosimetry was done by calorimetry. The data treatment, kinetic analysis, and data simulation were performed on a PDP 11/73 computer. In the $t^{-0.6}$ linearity tests, as shown in Figures 3 and 5, there are usually three different experimental curves from a single photomultiplier (Hamamatsu R1509 or Philips XP1003). They cover three different, partially overlapping time ranges and are from two different transient digitizers: a Tektronix 7912AD or 2440 and a Datalab DL912.

Room temperature pulse radiolysis was done at Tokai-mura (University of Tokyo)^{7a} with a LINAC for 28 MeV electrons, having a time resolution of 2 ns. The detection system was composed of a Hamamatsu R1328U-02 photodiode (rise time 60 ps) and a Tektronix SCD1000 transient digitizer (rise time 350 ps). Signal averaging was done by a NEC computer (PC-9801RA). For dosimetry a N₂O-saturated aqueous solution of 10 mM KSCN was used. (SCN)₂⁻ was observed at 472 nm with G = 6.1 (100 eV)⁻¹ and $\epsilon = 7580$ M⁻¹ cm⁻¹.^{7b}

Cell Window Signal. Although the quartz windows of the cell were of the highest purity (Suprasil), the production of color centers in the quartz windows introduced additional small absorptions. With lower temperature these cell signals increase. For temperatures lower than ca. -90 °C this signal remains constant during the observation time (most of our experiments are in this temperature range). At and near room temperature there is an initial, very fast decay (almost within the pulse duration), followed again by a constant absorption. For all experimental rate curves a constant absorption, due to the quartz defects, had to be deducted. The correction is particularly important for the rate curve analysis. It seriously affects the intercepts from the $t^{-0.6}$ linearity and therefore the free ion spectra and the experimental diffusion constant. In the preliminary report¹ this correction was not yet applied. For the

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For all temperatures and wavelengths used in the experiments, the cell signal (quartz defects) was determined with an empty cell, because it is difficult to find a liquid sample with no chemical transient signal. However, the effective dose on the window is smaller for a filled cell (the radiation field at the window is altered by the liquid). A dose correction factor Fwas determined separately to correct the empty cell dose to the filled cell dose on the window. This dose correction factor was determined with the following two chemical systems:

1. Water purged with argon, N_2O , or O_2 . As the water radiolysis for these systems is very well-known, the contribution from chemistry was calculated by our standard simulation software for aqueous systems.⁸ The remaining signal, after deduction of the chemistry contribution, must be due to the quartz window signal in the filled cell.

2. Methylcyclohexane purged with N₂O. From the transients produced in N₂O-saturated MCH, only the radical cation MCH⁺ and a small contribution from methylcyclohexene⁺ are absorbing for $\lambda > 350$ nm (details in this paper). By assuming that the free ion recombination is diffusion controlled (MCH⁺ actually disappears faster), the minimum time was estimated for the chemistry signal to become negligible. The remaining constant signal after that time was due to the quartz defect absorption.

From three aqueous systems and two MCH solutions the correction factor was determined at 450 and 550 nm. The resulting dose correction factor is $F = 0.64 \pm 0.08$. All empty cell signals then were corrected by this factor F to derive the cell signals for filled cells. These then were applied as a correction to all experimental rate curves.

Shock Wave Disturbances. The origin of shock waves in pulse radiolysis cells and their effect on the analyzing light beam have previously been discussed in detail, and methods to minimize the effect have been given.⁵ The amount of disturbance on the transient absorption signal is also dependent on the optical characteristics of the solution (most likely on the refraction index). Therefore it depends, e.g., on wavelength λ , on temperature, and on solute concentration. For the experiments with norbornadiene (NBD), reported in this paper, the interference with the shock wave pattern is particularly bad. As the patterns are correlated with the speed of sound, the shock signals can be identified at earlier times but get smeared out later on. In Figure 5a the shock signals are marked by the shaded area.

Chemicals. Methylcyclohexane (MCH, Fluka purum, >98% GC) was passed through a column of aluminum oxide, dried over molecular sieve A4, and then fractionated through a Fischer "Spaltrohrkolonne" with about 30 theoretical plates. N₂O (99%), CO₂ (99.5%), and argon (99.996%) were from PanGas Luzern. Norbornadiene (Aldrich, >99%), 2-propanol (Fluka puriss.), and cyclopropane (Merck-Schuchhardt, 99%) were used without further purification. At Tokai-mura methylcyclohexane from Dojindo (spectrograde "dotite") was used.

Simulation of Geminate Ion Kinetics

General. The geminate ion kinetics may be calculated from the Smoluchowski equation. The method to solve it for selective initial distributions for the primary pair of ions is summarized in reviews.⁹⁻¹¹ For long times (the tail of the geminate ion recombination kinetics) it has been shown theoretically that the probability of survival from the recombination of a single pair of oppositely charged ions can be described as a linear function of $t^{-0.5, 12-14}$ Another semiempirical formula is based on the findings that the dependence of the scavenging yield on the solute concentration is related to the dynamics of the ions through Laplace transformation.¹⁵ From the empirical Warman-Asmus-Schuler (WAS) equation for scavenging¹⁶ a semiempirical time dependence for the geminate ions was derived: $G(t) = G_{gi} \exp(\lambda t) \operatorname{erfc}(\lambda t)^{0.5,17}$ The most recent semiempirical formula, proposed by Van den Ende et al.,⁴ predicts a linear function of the ionic concentration with $t^{-0.6}$. We tried to fit the functions with $t^{-0.5}$, $t^{-0.6}$, and $\exp(\lambda t)$ erfc- $(\lambda t)^{0.5}$ to many of our experimental geminate ion kinetics. The $t^{-0.6}$ rate law was the only one to properly simulate our kinetics.

Recombination Kinetics for a Single Geminate Pair of Ions. The $t^{-0.6}$ rate law by Van den Ende et al. describes the probability of survival of the geminately recombining ions relative to the free ion yield:

$$\frac{G(t)}{G_{\text{fi}}} = 1 + 0.6 \left[\frac{r_c^2}{D}\right]^{0.6} t^{-0.6} = \frac{\text{absorbance}(t)}{\text{absorbance}(\infty)} = \frac{A(t)}{\text{IA}}$$
(1)

The absorption may have contributions from both types of ions (the sum of both absorption coefficients). Any plot of the absorbance A(t) against $t^{-0.6}$ should be linear. Its intercept IA for $t = \infty$ corresponds to the absorbance of the free ion yield. The slope divided by the intercept IA is called α . From this value, with the known Onsager radius r_c , an experimental diffusion constant can be derived: $D_{exp} = D^+ + D^-$.

The $t^{-0.6}$ rate law originally was said to hold for up to 3 times the free ion yield (3 times the intercept value).⁴ Today, from our several hundreds of experiments, it is clear, that the law holds for much earlier times (e.g., up to more than 10 times the free ion yield). Whenever there appeared a deviation from linearity, a chemical reason was eventually found for this deviation. In our low-temperature range (127–183 K) the $t^{-0.6}$ rate law was correct for t > ca. 100 ns. Theoretical support for the $t^{-0.6}$ rate law was recently given by Barczak and Hummel.¹⁸ They compared numerical calculations based on multi-ion pairs with empirical simulations based on a linearity with xt^{-y} . They found a best fit for x = y = 0.6.

Extended $t^{-0.6}$ Rate Law To Include Ionic Reactions. There are two limiting rate laws. At very early times, the geminate recombination is between the primary ions only:

$$\frac{A_{\text{prim}}(t)}{\text{IA}} = 1 + \alpha t^{-0.6} \text{ with } \alpha = 0.6 \left(\frac{r_c^2}{D_{\text{prim}}}\right)^{0.6} \text{ and IA} = A_{\text{nrim}}(\infty) (2)$$

At very late times the geminate recombination is between the secondary ions only:

$$\frac{A_{\text{sec}}(t)}{\text{IB}} = 1 + \beta t^{-0.6} \text{ with } \beta = 0.6 \left(\frac{r_{\text{c}}^2}{D_{\text{sec}}}\right)^{0.6} \text{ and } \text{IB} = A_{\text{sec}}(\infty) (3)$$

The change over from the primary to the secondary pair of geminate ions is due to a first-order reaction (e.g., fragmentation) or to a pseudo-first-order scavenging process.

In analogy to our treatment for the CCl_4^+ fragmentation in liquid CCl_4^{19} the *primary ion kinetics* with k_1 as a first-order or pseudo-first-order rate constant is therefore given by

$$\frac{A_{\text{prim}}(t)}{\text{IA}} = (1 + \alpha t^{-0.6}) e^{-k_1 t}$$
(4)

The expression is identical to the one derived for the disap-



Figure 1. The principle of $t^{-0.6}$ kinetic simulations, for an arbitrary change from primary to secondary geminate ions. The actual time scale is added at the bottom of the figure: early times are stretched, and late times are compressed. The curves are marked by the number of the corresponding equation. Parameter fitting (see arrows) normally starts with the easily observable linearity of the *secondary* pairs of ions (3) $\rightarrow \beta$, IB. It is followed by fitting k_1 of the ionic reaction in the region of bending away from (3). Then the *primary* kinetics is adjusted (2) $\rightarrow \alpha$, IA. (6) simulates the total absorbance A. For details see text.

pearance of CCl₄⁺ in the earlier paper,¹⁹ except that $exp(\lambda t)$ erfc(λt)^{0.5} (model of Rzad et al.¹⁷) is replaced by the rate law 1 + $\alpha t^{-0.6}$.

The secondary geminate ion kinetics is approximated by

$$\frac{A_{\text{sec}}(t)}{\text{IB}} = (1 + \beta t^{-0.6})(1 - e^{-k_1 t})$$
(5)

The sum of the primary and secondary ion absorbances then simulates the experimental time profile

$$A(t) = A_{\text{prim}}(t) + A_{\text{sec}}(t)$$
(6)

Since the secondary ions are produced at a variety of positions and times, the term $(1 - e^{-k_1 t})$ in eq 2 is not exact. Better calculations were published by Rzad et al.¹⁷ with the function $\exp(\lambda t) \operatorname{erfc}(\lambda t)^{0.5}$ and by Tachiya²¹ relating to the $t^{-0.5}$ rate law. As neither description for the geminate ion recombination satisfied our experimental curves, the $t^{-0.6}$ rate law was preferred and some inaccuracy for the secondary geminate pair (eq 5) was accepted. The error introduced cannot be very large, as all simulations with eqs 4–6 fitted very well to the experimental rate curves. Furthermore the rate constants k_1 derived from the simulation are quite constant over the λ range for the ionic absorption, although the relative absorbances from primary and secondary ions may change drastically.

 $t^{-0.6}$ Plots. The $t^{-0.6}$ kinetic plots are unusual to interpret owing to the reversed scale: short times correspond to large $t^{-0.6}$ values. Furthermore, early times are extremely stretched, whereas late times are strongly compressed (see Figure 1). Since the slope is proportional to α , it is also correlated to the inverse of the diffusion coefficient D. Therefore fast processes (high D) display a small slope; slow processes, a large slope.

If the mobilities of the primary and secondary ions are the same, the slopes may still alter through changed ion absorption (different absorption coefficients ϵ_i). The effect is linked to the intercept, which is proportional to $G_{fi}(\epsilon^+ + \epsilon^-)$.

The $t^{-0.6}$ linearity simulates the geminate ion kinetics only. The free ion recombination therefore shows up as a deviation from linearity at late times. This is seen in Figure 3 for $t^{-0.6} < 0.2 \ \mu s^{-0.6}$ or t > ca. 15 μs (143 K).

The parameter fitting for geminate ion kinetics with an overlying ionic reaction should follow the sequence illustrated in Figure 1: (1) The secondary ion kinetics (β value and intercept IB) is determined directly from the linearity at late times. (2) The deviation from that linearity toward earlier times is primarily dependent on k_1 . (3) The very early part then is defined by the primary ion kinetics (α value and intercept IA). If α is known from other experiments, then the fitting determines IA or vice versa. If both parameters are not known, the parameter determination is difficult.

The accuracy of the α values and derived diffusion constants D_{exp} from the kinetic analysis with the $t^{-0.6}$ rate law is dependent on the error limits of the rather small intercepts. This is due to the very small free ion yield for nonpolar solvents at low temperatures (see below). The correction for the quartz defects in the cell window therefore becomes very important for the intercept determination. Even though the slope of the $t^{-0.6}$ plot is quite accurate, an assumed 10% error in the intercept IA initiates a 10% error in α and correspondingly a 17% error for the diffusion constant D.

Results

The 570 nm Band. On pulse radiolysis of a solution of MCH, saturated with N₂O (0.118 M), weak absorptions were detected at low temperatures in the visible wavelength range (typically from 400 to 750 nm, Figure 2a). There are two maxima, one at 570 nm and the other at 450 nm. The 450 nm band is considered to be a small contribution, because in the many chemical systems studied, it is not always as pronounced as seen in Figure 2. The decay kinetics throughout the visible is neither of first order nor of second order, however, it fits to a linear relationship with $t^{-0.6}$ (Figure 3). This is true for the complete λ range from ca. 400 to 750 nm.

The absorption in the visible therefore must be due to ions, which recombine geminately in the time range of linearity ($t^{-0.6} > ca. 0.2$). The deviation for $t^{-0.6} < 0.2$ ($t > 15 \mu s$) is due to the free ion recombination, which is not covered by the $t^{-0.6}$ kinetic law.

Scavenger Studies. The anions N_2O^- and O^- are not absorbing in the visible λ range. Experiments with MCH saturated with CO₂ instead of N₂O (0.071 M CO₂²⁰) gave identical results (Figure 2b). The positive ion therefore appears to be responsible for the 570 nm absorption. The following positive scavengers were applied to the N₂O-saturated MCH solution (mostly at 143 K):

Cyclohexene. In a solution of 10 mM cyclohexene the wellknown^{22.23} and strong bands for c-hexene⁺ (450 nm) and (chexene)₂⁺ (ca. 780 nm) were observed. In a 100 mM c-hexene solution the monomer cation band at 450 nm is much weaker, in favor of a very strong dimer cation band at 780 nm. Cyclohexene is known to scavenge the positive charge by charge transfer.

Cyclopropane. Cyclopropane and N₂O are both gases. The solution therefore was prepared by separately saturating two solutions with N₂O or cyclopropane and then mixing the master solutions by 1:1. One observes the well-known, strong bands for c-propane⁺ at 450 nm and (c-propane)₂⁺ at 800 nm.²⁴ Cyclopropane is expected to scavenge the positive charge through charge transfer.



Figure 2. Liquid methylcyclohexane (MCH) at -130 °C (143 K) (a) saturated with N₂O (0.118 M) or (b) saturated with CO₂ (0.071 M²⁰). The transient spectra are normalized to 100 Gy and shown for selective times. The spectra marked ∞ correspond to the free ion absorption, as determined by the intercept from the $t^{-0.6}$ linear plots. A = absorbance.

2-Propanol. 100 mM 2-propanol (in N₂O-saturated MCH) removed most absorption in the visible. The remaining very weak background absorption has no peak at 570 nm. 2-Propanol is scavenging by proton transfer.²⁵

The above scavenger studies indicate that there is a positive ion acting as precursor. However, only with 2-propanol it is possible to say that the 570 nm band was suppressed. To find support for the 570 nm band to be the direct precursor to the scavenger cation (S⁺), norbornadiene (NBD) of varied concentration was used as scavenger. The decay of the 570 nm transient and the buildup of the well-known absorption for the solute radical cation (NBD⁺) ($\lambda_{max} = 650$ nm) was simulated by the extended $t^{-0.6}$ kinetic law (eqs 4–6) and compared with the experimental rate curves.

Norbornadiene (NBD) at 133 K. With a high concentration of 100 mM norbornadiene in MCH the NBD⁺ spectrum²⁶ is detected (Figure 4). Its decay kinetics clearly follows the $t^{-0.6}$ kinetic law (Figure 5a). At early times a small buildup for the 650 nm band of NBD⁺ can be detected. If the 570 nm transient should be the direct precursor of NBD⁺, then the following scheme of geminate ion recombination has to be tested:



Figure 3. $t^{-0.6}$ plot of the rate curve at 550 nm for N₂O-saturated MCH at -130 °C (143 K). (A = absorbance). Parameters are $\alpha = 3.05 \ \mu s^{0.6}$, intercept IA = 1.85×10^{-3} .



Figure 4. Transient spectra for an N₂O-saturated liquid solution of 100 mM norbornadiene (NBD) in methylcyclohexane (MCH) at -140 °C (133 K). Absorbance A normalized to 100 Gy.



The corresponding kinetic simulation with the extended $t^{-0.6}$ kinetic law should reproduce the experimental rate curves with different NBD concentrations. With lower concentrations of NBD the initial buildup becomes more pronounced. Experiments were performed for 6, 3, and 1 mM NBD at $\lambda = 550$ and 650 nm. Furthermore complete spectra from 525 to 700 nm were recorded for 100, 0.4, and 0.1 mM NBD. The system of lowest concentration is indistinguishable from solutions without NBD, as 0.1 mM solute is not scavenging geminate ions. It was used to derive the data for the primary pair of ions (570 nm transient + N₂O⁻). From the data for the highest concentration (100 mM NBD) the kinetic data for the secondary



Figure 5. Methylcyclohexane (MCH), N₂O saturated, with *x* mM NBD at -140 °C (133 K): Absorbance *A* at 650 nm with computer simulation. The straight lines are marked with the corresponding primary or secondary pair of geminate ions. (a) The two limiting cases, 0 and 100 mM NBD. For 100 mM NBD a final buildup is seen at early times (top of figure). The typical shock wave disturbances are marked here as shaded area. (b) The simulation for 6, 3, and 1 mM NBD. For clarity reasons the line for the secondary ions (NBD⁺ + N₂O⁻) is shown for 6 mM NBD only.

pair of ions were derived. From the intermediate concentrations the pseudo-first-order rate constants for scavenging are derived. By careful iteration throughout all 47 experiments the best set of data was determined. The result is exemplified in Figure 5 for $\lambda = 650$ nm, where the NBD⁺ is dominating. However the fitting also included the rate curves at 550 nm, where the 570 nm precursor is dominating.

For the primary ions α was derived by dividing the experimental slope by the intercept (after correction for the cell signal). The α values appear to be quite constant from 400 to 750 nm. Therefore all α values were averaged to yield $\alpha(133 \text{ K}) = 4.5 \,\mu\text{s}^{0.6}$. In the region around 450 nm there is a hint for increased α values, explainable with the perturbation from the small 450 nm band; however, the deviation is not significant.

TABLE 1: Rate Data for the MCH $-N_2O-NBD$ System at 133 K

[NBD], mM	$\beta, \mu s^{0.6}$	D_{exp} , $cm^2 s^{-1}$	$k_2, \mathbf{M}^{-1} \mathbf{s}^{-1}$
100	26.7	5.4×10^{-8}	·
6	22.0	7.5×10^{-8}	1.8×10^{8}
3	21.8	7.6×10^{-8}	1.4×10^{8}
1	20.0	8.8×10^{-8}	2.5×10^{8}
0.4	20.0	8.8×10^{-8}	1.8×10^{8}
0.1	20.5	8.4×10^{-8}	
error limit (estimated)	$\pm 5\%$	$\pm 10\%$	±25%

From $\alpha = 4.5 \,\mu s^{0.6} \,(133 \text{ K})$ and the Onsager radius r_c (calculated to be 55.1 nm) the sum of the diffusion constants of the two geminate ions can be derived:

$$D_{\rm exp}(133 \text{ K}) = D^+ + D^- = (1.06 \pm 0.2) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$$

From the viscosity η of the solvent, a theoretical diffusion constant D_{th} for molecules of radius *r* can be calculated, based on the Stokes-Einstein formula:

$$D_{\rm th} = \frac{kT}{6\pi r\eta}$$

By extrapolating published data²⁷ the viscosity is determined to be $\eta_{\text{MCH}}(133 \text{ K}) = 1.26 \text{ Pa s}$. The molecular radii are estimated to be $r(\text{MCH}^+) \approx 3 \text{ Å}$ and $r(N_2O^-) \approx 2 \text{ Å}$.²⁸ The corresponding theoretical values are

$$D_{\text{th}}^+(133 \text{ K}) = 2.58 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$$

 $D_{\text{th}}^-(133 \text{ K}) = 3.86 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$

As these values are much smaller than D_{exp} , it is concluded that the positive species with $\lambda_{max} = 570$ nm moves about 400 times faster than diffusion:

$$D_{\rm exp}^+(133 \text{ K}) \approx 400 D_{\rm th}^+(133 \text{ K})$$

The intercept spectrum for an NBD free solution corresponds to the spectral sum of the free ions (see Figure 2). Because neither N_2O^- or O^- is absorbing in the visible, the spectrum is the one of the positive ion only. This spectrum is quite similar to the early geminate ion spectra. During the observation time the geminate cations therefore are neither reacting nor fragmenting.

From the secondary ion kinetics (the system with 100 mM NBD) the geminate ion recombination between NBD⁺ and N₂O⁻ (or O⁻) is observed. From the linear plot against $t^{-0.6}$, the slope is divided by the intercept (corrected for the cell signal) to derive the β value. For the high concentration of 100 mM NBD one finds

$$\beta(133 \text{ K}, 100 \text{ mM}) = 26.7 \,\mu\text{s}^{0.6}$$

The rate constants k_2 for the reaction "570 nm" + NBD are determined from simulating the intermediate concentrations of NBD. The results are listed in Table 1. It turned out that the β values are concentration dependent. Higher β values (at higher concentrations of NBD) mean slower ion recombination. Therefore the viscosity of the solution appears to be increasing with higher solute concentration. This is not unexpected for such supercooled liquids. The most characteristic value for D_{exp} and k_2 therefore should be derived from the low concentration data:

$$\beta(133 \text{ K}) = 20.0 \pm 1.0 \,\mu\text{s}^{0.6}$$

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temp, K	$N_{\rm s}/N_{\rm c}$	α , μ s ^{0.6}	r _c , nm	$D_{\rm exp},{\rm cm}^2{\rm s}^{-1}$	η , ^b Pa s	$D_{\rm th}^{+,c} {\rm cm}^2 {\rm s}^{-1}$	$D_{\rm th}^{-,c} {\rm cm}^2 {\rm s}^{-1}$	D_{\exp}^{+}/D_{th}^{+d}		
N ₂ O-Saturated MCH										
293	1/6	0.145	27.8	8.24×10^{-5}	10-3	7.2×10^{-6}	1.1×10^{-5}	10		
153	1/3	2.04	48.3	3.03×10^{-6}	0.125	2.9×10^{-8}	4.3×10^{-8}	103		
143	6/69	3.09	51.3	1.76×10^{-6}	0.366	9.4×10^{-9}	1.4×10^{-8}	186		
138	1/7	3.87	53	1.26×10^{-6}	0.654	5.2×10^{-9}	7.8×10^{-9}	241		
133	3/25	4.44	55.1	1.07×10^{-6}	1.260	2.6×10^{-9}	3.9×10^{-9}	410		
CO ₂ -Saturated MCH										
143	3/48	2.94	51.3	1.86×10^{-6}	0.366	9.4×10^{-9}	1.4×10^{-8}	196		
133	2/13	4.51	55.1	1.04×10^{-6}	1.260	2.6×10^{-9}	3.9×10^{-9}	399		
129	1/21	4.93	56.4	9.51×10^{-7}	2.26	1.4×10^{-9}	2.1×10^{-9}	678		
128	1/3	5.09	56.8	9.14×10^{-7}	2.83	1.1×10^{-9}	1.7×10^{-9}	830		
127	2/2	5.27	57.2	8.75×10^{-7}	3.54	8.8×10^{-10}	1.3×10^{-9}	993		

^{*a*} r_c = Onsager Radius, η = Viscosity (mPa s = cP), D = Diffusion Constant, N_s/N_c number of chemical systems/number of rate curves analyzed, to document the reliability. ^{*b*} Viscosity, extrapolated from ref 27. ^{*c*} The radii estimated from ref 28: $r(MCH^+) = 3 \text{ Å and } r(N_2O^-) = 2 \text{ Å}$. ^{*d*} $D_{exp}^+ = D_{exp} - D_{th}^-$.

corresponding to

$$D_{\rm exp} = D^+ + D^- = (8.8 \pm 0.7) \times 10^{-8} \,{\rm cm}^2 \,{\rm s}^{-1.29}$$

and

$$k_2 = (1.8 \pm 0.5) \times 10^8 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}$$

For a diffusion-controlled scavenging, the rate constant should be

$$k_{\text{diff}}(133 \text{ K}) = 2.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

The experimental k_2 value, however, is about 80 times faster. This again makes it clear that the high-mobility cation, absorbing at 570 nm, is the precursor. The scavenging results with NBD therefore agree with the proposed reaction scheme. The 570 nm species is a direct precursor to the radical cation NBD⁺. The 570 nm transient must be the solvent radical cation MCH⁺.

Temperature Dependence of the MCH⁺ Mobility. The lowest accessible temperature was determined by the stability of the supercooled liquid. For the N₂O-saturated solutions this was about 133 K, for CO₂-saturated solutions 127 K. The upper temperature was limited by the time resolution of the technique. For temperatures higher than 153 K the observation of the geminate ions was lost within the 50 ns electron pulse. Therefore room temperature experiments were performed at the installation at Tokai-mura of the University of Tokyo. Their time resolution was ca. 1 ns. Due to the small available dose of ca. 17 Gy, signal averaging was used to reduce the noise contribution. A typical rate curve, plotted against $t^{-0.6}$ is shown in Figure 6.

For each chemical system (freshly prepared solution) a mean α value was derived. For the systems at 143 and 133 K the complete λ range from ca. 350 to 700 nm was used. The mean α value then was held fixed for all λ , to derive the spectrum of the free ion contribution (intercepts from the $t^{-0.6}$ linearity). The free ion spectra are generally rather weak (due to low $G_{\rm fi}$). However, due to the linear regression (with $t^{-0.6}$) they are often better defined than the direct transient spectra at earlier times. Free ion spectra for N₂O- and CO₂-saturated MCH are included in Figure 2.

Table 2 summarizes the α values. It also lists the number of chemical systems studied and the number of rate curves analyzed. The systems with N₂O and CO₂ are very similar, and the α values and intercept spectra for the same temperature are indistinguishable within experimental error. For each α value, together with the Onsager radius r_c (defined by the solvent only), an experimental diffusion constant $D_{exp} = D^+ + D^-$ is derived



Figure 6. $t^{-0.6}$ plot of the transient absorbance A for the MCH⁺ + N₂O⁻ geminate recombination at room temperature (20 °C, 293 K), as measured at 570 nm. (Experiment at University of Tokyo, time resolution ca. 1 ns).

(Table 2). An Arrhenius plot of these D_{exp} is given in Figure 7. The activation energy is

$$E_{\rm act} = 8.9 \pm 0.3 \text{ kJ/mol}$$

The deviations observed for temperatures lower than 133 K (the CO_2 -saturated MCH) probably relate to the difficulties with the strongly supercooled liquids.

Discussion

The 570 nm Assignment. From the scavenger studies it must be concluded that the 570 nm band is due to a cationic species. From the experiments with norbornadiene (NBD), the 570 nm species appears to be a direct precursor to the solute radical cation NBD⁺. From the simulation of the rate curves, the buildup rate k_2 of NBD⁺ is about 80 times faster than diffusion, corresponding to the high mobility of the 570 nm species. This 570 nm band is also a precursor to other radical cations from solutes like *cis*-Decalin, *trans*-Decalin, and adamantane.³⁰ They all are able to accept the positive charge by charge transfer from the solvent radical cation MCH⁺, as their ionization potentials are all lower than the one for MCH. Proton transfer is unable to explain the formation of the radical cation NBD⁺, and the 570 nm band cannot be assigned to a protonated MCH, as theory



1/T × 1000/K **Figure 7.** Arrhenius plot for the MCH⁺ diffusion constant D_{exp}^+ , derived from the α values in (+) N₂O-saturated or (□) CO₂-saturated MCH. The activation energy is 8.9 ± 0.3 kJ/mol. Also shown is the theoretical diffusion constant D_{th}^+ derived from the solvent viscosity η^{27} and the Stokes-Einstein relation (see Table 2).

6

7

я

5

Δ

-55

З

is not predicting an absorption in the visible λ range.³¹ It is therefore concluded that the 570 nm transient must be due to the solvent radical cation MCH⁺.

The High Mobility. Table 2 includes the theoretical diffusion constants $D_{\rm th}^+$ and $D_{\rm th}^-$, based on molecular movement in the solvent of viscosity η (Stokes–Einstein formula), with the estimated radii to be $r^+(\rm MCH^+) \approx 3.0$ Å and $r^-(\rm N_2O^-) \approx 2.0$ Å²⁸). Figure 7 also shows the temperature dependence of $D_{\rm th}^+$, which follows the temperature dependence of the viscosity η . With lower temperature the ratio of the mobility of the positive charge to the diffusional rate becomes larger: at room temperature the radical cation MCH⁺ moves about 10 times faster than diffusion, at 133 K, however, ca. 400 times faster.

Comparison with Conductivity Data. Warman et al. published a value for the conductivity of the positive charge in MCH at room temperature:³²

$$\mu^+ = 2.6 \times 10^{-3} \,\mathrm{cm}^2 \,\mathrm{V}^{-1} \,\mathrm{s}^{-1}$$

The anion mobility (in our case N₂O⁻, O⁻, or CO₂⁻) is taken from Warman's values for $^{1}/_{2}\mu(S^{+},S^{-})$, which represents diffusional conductivity. With $\mu^{-} = 0.45 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ the total conductivity is

$$\mu^{+-} = 3.05 \times 10^{-3} \,\mathrm{cm}^2 \,\mathrm{V}^{-1} \,\mathrm{s}^{-1}$$

With $D = \mu kT/e$ the corresponding diffusion constant from conductivity is derived:

$$D^{+-} = 7.71 \times 10^{-5} \,\mathrm{cm}^2 \,\mathrm{s}^{-1}$$

Our experimental value at room temperature (295 K) from optical absorption is

$$D_{\rm exp} = 8.24 \times 10^{-5} \, {\rm cm}^2 \, {\rm s}^{-1}$$

 TABLE 3: Intercepts, Representative of the Free Ion Yield in MCH^a

	inte					
temp, K	N ₂ O-sat. MCH	N_{s}^{b}	CO ₂ -sat. MCH	Ns ^b	mean IA	$G_{\rm fi},$ (100 eV) ⁻¹
295	4.2	1			4.2 ± 0.2	0.1233
153	2.3	3			١	
143	1.90 ± 0.33	5	2.30 ± 0.50	3		
138	1.40	1			2.1 ± 0.4	0.060°
133	2.17 ± 0.50	3	2.10 ± 0.30	2	1	± 0.015
127			2.7	2]	

^{*a*} 2 cm optical pathlength, normalized to 100 Gy. ^{*b*} N_s = number of chemical systems studied. ^{*c*} $G_{\rm fi}$ calculated from the value at 295 K³³ by the ratio of the mean IA.

These values are identical within 7%. This strongly indicates that the two techniques, conductivity and optical spectroscopy, are observing the same positive species, the radical cation MCH⁺. The earlier proposal³ that the fast conductivity signal in MCH should be due to proton transfer becomes rather unlikely.

The Free Ion Yield at Low Temperature. The intercepts of the many $t^{-0.6}$ linearity plots are due to the free ion yields $G_{\rm fi}$. As they are defined by the solvent only, intercepts can be compared for all MCH solutions. Table 3 summarizes the intercept absorbances for 570 nm. Within experimental error limits there is no difference between N₂O- or CO₂-saturated solutions. Neither is there any significant trend for the lowtemperature values (127–153 K) detectable. The room temperature value, however, is much higher. With the assumption that the absorption coefficient remains independent of temperature, the free ion yield in methylcyclohexane (MCH) for temperatures of 127–153 K is calculated to be 2 times smaller than at room temperature:

$$G_{\rm fi}(127-153 \text{ K}) = 0.06 \pm 0.015 (100 \text{ eV})^{-1}$$

As it was found (see below) that a small fraction of the free ions is lost to the olefinic cation ($\lambda_{max} = 450$ nm), due to fragmentation of an excited precursor cation, this $G_{\rm fi}$ determination is only correct if the corresponding competition (fragmentation against N₂O quenching) is not shifted with temperature. The intercept ratio for 450-570 nm, however, is found to be almost independent of temperature.

From the $G_{\rm fi}$ value at room temperature ($G_{\rm fi}(20 \,^{\circ}{\rm C}) = 0.12^{33}$)) and the corresponding intercept, the absorption coefficient ϵ for MCH⁺ at $\lambda_{\rm max}$ can be calculated. Due to the small loss to the olefinic cation ($\lambda_{\rm max} = 450 \,$ nm), the derived ϵ represents a minimum value:

$$\epsilon_{570}(\text{MCH}^+) \ge 2300 \text{ M}^{-1} \text{ cm}^{-1}$$

Argon-Saturated MCH: Olefinic Cations Produced from Unquenched Radical Cations. To derive α values and diffusion constants *D* from the linearity with $t^{-0.6}$ the very good values for the slope have to be divided by the less accurate, small intercept. α and *D* therefore are of limited accuracy. The only way to increase the intercepts is to choose ions of large absorption coefficients ϵ . With this idea in mind, experiments with neat MCH (actually argon-saturated MCH) were studied. The negative charge then appears as a solvated electron with a strong absorption toward the near infrared. The results were unexpected, as no radical cation MCH⁺ could be detected on a microsecond time scale or later. Rather an absorption band with $\lambda_{max} = 450$ nm appeared, which we eventually assigned to the olefinic cation (methylcyclohexene⁺). There is no fast mobility any more for this cation. The geminate ion recombination is now between the olefinic cation and the solvated electron e_{solv}^- . It appears that without N₂O or CO₂ an initial excited state of the radical cation remains unquenched and quickly fragments to the olefinic cation. In the presence of quenchers (N₂O or CO₂) the olefinic cation is strongly suppressed; however, a small contribution at 450 nm remains, as seen in Figure 2. Detailed proof for that interpretation will be published elsewhere.³⁴

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