Anion of Tetrachloroethane (Tetra): Fragmentation and Geminate Ion Kinetics in Liquid Methylcyclohexane (MCH)

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In the context of studies on the influence of the anion lifetime on the geminate ion kinetics, 1,1,1,2- and 1,1,2,2-tetrachloroethane (1112-Tetra and 1122-Tetra) were studied as solutes in liquid methylcyclohexane (MCH) at low temperatures (133−183 K). The two isomers serve as examples of long anion lifetime. The analysis of the pulse radiolysis data was based on the $t^{-0.6}$ semiempirical law for geminate ion kinetics. The visible band with $\lambda_{max} = 450$ or 430 nm is shown to be due to the anion of 1112-Tetra or 1122-Tetra, respectively. Its kinetics relates to three consecutive geminate pairs of ions, due to two ionic reactions: (a) *The fast process* represents the cationic mechanism: the precursor cation M^{+*} relaxes (or isomerizes) to the high mobility ion MCH^+ (k_r) and simultaneously fragments (k_f) to a diffusional methylcyclohexene$^+$ (MCHene$^+$). The total M^{+*} decay ($k_{tot} = k_r + k_f$) produces mixed cations (MCH^+,MCHene$^+$). (b) *The slow process* is due to the anion fragmentation (k^-) from Tetra$^-$ to $Cl^- + R^\bullet$, with $\tau^- = 13.7$ or 20.0 μs (143 K) for 1112- or 1122-Tetra, respectively. The fragment radical $R^\bullet$ is freed too late to allow scavenging of positive charge. *The three geminate pairs of ions* are (M^{+*}/Tetra$^-$), (MCH^+,MCHene$^+$/Tetra$^-$), and (MCH^+,MCHene$^+$/Cl^-). All ions (except Cl^-) contribute to the optical absorption. The *rate constants* k_{tot} and k^- are both independent of the concentration of Tetra. For k_{tot} this means that M^{+*} decays in a fixed ratio of k_f to k_r. This is in contrast to previous findings with N_2O or $CHCl_3$ but corresponds to our recent proposal that M^{+*} appears to represent some isomer of MCH^+ in a higher energy state (or of higher ionization potential). The *anion fragmentation* rate for 1112-Tetra is $k^-(143\ K) = (7.3 \pm 0.6) \times 10^4\ s^{-1}$ with $E_{act} = 17.8$ kJ/mol and log $A = 11.2$. For 1122-Tetra it is $k^-(143\ K) = (5.0 \pm 1.0) \times 10^4\ s^{-1}$ with $E_{act} = 16.9$ kJ/mol and log $A = 10.9$. The *free ion intercepts*, from the $t^{-0.6}$-simulations, reveal for all geminate pairs with Tetra$^-$ a strong dependence on the Tetra concentration [T], eventhough complete electron scavenging was ascertained. This is explained by the formation of dimer anions T_2^- through an equilibrium $T^- + T \rightleftharpoons T_2^-$. The absorption at 450 nm (or 430 nm) then is due to T_2^- (most likely a charge resonance transition ($T \leftarrow T^-$)). For the initial geminate pair (M^{+*}/Tetra$^-$), the free ion intercept was smaller than the one for Tetra$^-$ alone (actually T_2^-). As this result was based on the assumption that M^{+*} and MCH^+ have the same mobility, this now reveals that the precursor cation M^{+*} must have at least a 9 times higher mobility than MCH^+.

I. Introduction

In the adjacent paper[1] (and its preceding one[2]) the effect of the anion lifetime on the geminate ion kinetics is discussed for chlorocarbons in liquid methylcyclohexane (MCH). In the context of that paper, tetrachloroethane (Tetra) served as an example of long anion lifetime. Its results yet revealed additional insights into the behavior of cations and anions in general, far beyond the effect of anion lifetime on geminate ion kinetics. Therefore, the results for tetrachloroethane are discussed in this separate paper. From the analysis of the geminate ion kinetics for tetrachloroethane, it has been concluded that the mobility of the cationic precursor M^{+*} must be higher than the one of MCH^+—not the same, as was previously assumed. Furthermore, to explain the concentration dependences of the free ion intercepts, the formation of dimer anions through the equilibrium Tetra$^-$ + Tetra $\rightleftharpoons$ Tetra$_2^-$ is proposed. Details follow in this paper.

II. Experimental Section

A. Methods. The technique of pulse radiolysis with a Febetron 705 accelerator (Physics International) for 30 ns pulses of 2 MeV electrons has been used as reported in the adjacent paper.[1] Experiments with methylcyclohexane (MCH) as solvent were typically performed in the temperature range from 133 to 183 K in the liquid state. A typical dose was between 50 and 120 Gy. All data usually are normalized to 100 Gy. All the experimental signals were corrected for the cell window signal (quartz defects).[3] The origin of shock waves in pulse radiolysis cells and the method to minimize the effect have also previously been discussed in detail.[3,4]

B. Chemicals. Methylcyclohexane (MCH) (Fluka purum, >98% GC) was passed through a column of aluminum oxide, dried over molecular sieves A4, and then fractionated through a Fischer "Spaltrohrkolonne" with about 30 theoretical plates. 1,1,1,2-Tetrachloroethane (1112-Tetra, CCl_3CH_2Cl) and 1,1,2,2-

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tetrachloroethane (1122-Tetra, $CHCl_2CHCl_2$) from Aldrich (>99%) and N_2O from PanGas, Luzerne CH (99%), were used as received.

III. Method of Data Analysis

The simulation of the rate data is described in detail in the adjacent paper.[1] The basis is the semiempirical $t^{-0.6}$ kinetic law for the geminate ion recombination, as initiated by van den Ende et al.[5] It describes the probability of survival of the geminately recombining ions relative to the free ion yield:

$$\frac{G(t)}{G_{fi}} = 1 + \alpha t^{-0.6} = \frac{\text{absorbance}(t)}{\text{absorbance}(\infty)} = \frac{A(t)}{IA}$$

$$\text{with} \quad \alpha = 0.6\left[\frac{r_c^2}{D}\right]^{0.6} \quad (1)$$

where α is the mobility value and $IA = A(\infty)$ is the free ion intercept.

Any plot of the absorbance $A(t)$ against $t^{-0.6}$ should be linear. Its intercept IA for $t = \infty$ ($t^{-0.6} = 0$) corresponds to the absorbance of the free ion yield. The slope divided by the intercept IA is called α, a mobility value (or β, γ, etc. for other geminate pairs). From this value, with the known Onsager radius r_c, an experimental diffusion constant can be derived: $D_{exp} = D^+ + D^-$.

Theoretical support for the $t^{-0.6}$ rate law was given by Bartczak and Hummel.[6,7] We have given experimental support [2,3,8−13] and could derive some experience about the validity range: for low-temperature studies in liquid MCH (e.g. 143 K) the $t^{-0.6}$ kinetic law holds at least to $t^{-0.6} = 4.0$ (t ⩾ 100 ns). In this range all deviations from the $t^{-0.6}$ linearity had a chemical reason and could be explained.

For this purpose the theory was extended to cover ionic reactions, which are overlapping with the geminate ion recombination kinetics. It also covers combinations of ionic reactions (parallel or consecutive, for positive and/or negative ions) and is able to simulate ion recombinations leading to products, which are optical absorbers. In this paper the mathematical equations needed are quoted from the adjacent paper,[1] referring to eqs 1−12.

IV. Results

In MCH solutions the initial process usually corresponds to the mechanism of the high mobility cations: with the precursor cation M^{+*} relaxing (or isomerizing) into the high mobility radical cation MCH^+ (k_r) and, in parallel, fragmenting (k_f) into the diffusional cation of methylcyclohexene ($MCHene^+$).[3,8,9,11−13] The solvated electron is scavenged by the solute Tetra (T) to form its anion $Tetra^-$ (or T^-), which is expected to have a long fragmentation lifetime.[1] The solute Tetra might also influence the relative yields of MCH^+ and $MCHene^+$. Scheme 1 represents the expected mechanism, where $k_r = k_0 + k_2[T]$ includes a possible concentration dependence. It corresponds to the finding with chloroform as solute.[8] To test Scheme 1, the chemical systems of Table 1 were studied in detail with both isomers.

All observations and discussions will be limited to the time range after completion of electron scavenging by Tetra, taken as 99% scavenged (anchor point[14] for e^-_{solv} + T). A rate constant k_e for electron-scavenging was derived from the known diffusion constants at 143 K: $D(e^-_{solv}) = 1.6 \times 10^{-6}$ cm^2 s^{-1} (ref 9) and D(Tetra) ≈ $D(MCH^+)_{theor} = 9.4 \times 10^{-9}$ cm^2 s^{-1} (the theoretical value for diffusional mobility of MCH^+ (ref 3).

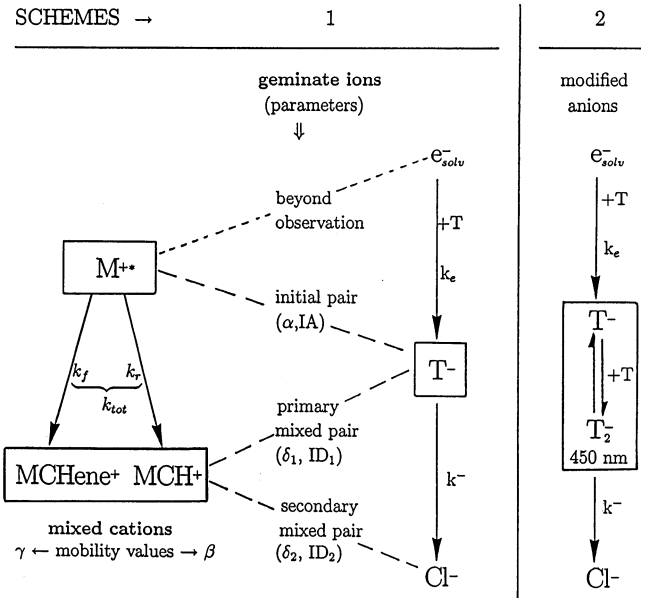

TABLE 1: Chemical Systems Studied for the Two Isomers of Tetra in MCH

system	concentration	temp/K	λ/nm	comments
		1,1,1,2-Tetrachloroethane (1112-Tetra)		
A	5.3−530 mM	143	450, 570	conc variation
B	0.2 M	143	350−650	transient spectra
C	0.2 M	143	350−650	with N_2O sat. (0.118 M)
D	0.2 M	133−163	450	temp variation
		1,1,2,2-Tetrachloroethane (1122-Tetra)		
E	0.2 M	143	350−750	transient spectra
F	0.2 M	153	450	with N_2O sat. (0.118 M)
G	0.2 M	143−183	450	temp variation

The reactant radii were chosen to be 0.2 or 0.3 nm for e^-_{solv} or Tetra, respectively. Therefore, the diffusional rate constant for electron scavenging at 143 K is $k_e = 4.8 \times 10^8$ M^{-1} s^{-1}. This then allows us to calculate the corresponding "anchor point" AP (ref 14) for the $t^{-0.6}$ plots: $AP_e(1\%) = 0.4 \times (k_e[T] \times 10^{-6})^{0.6}$. For all concentrations [Tetra] ⩾ 90 mM our complete experimental time window (t ⩾ 100 ns, means $t^{-0.6} \leq 4.0\ \mu s^{-0.6}$) is unaffected by the scavenging process. For lower concentrations the observation window was reduced correspondingly.

A. Initial Spectral Observations. The transient spectra as shown in Figure 1 for both Tetra isomers uniformly decay over the band displayed. There is no λ_{max} shift with time, as found for other halocarbons (hexa- and pentachloroethane[1]). By saturating with N_2O the earliest transient spectrum is reduced by about 10%, without changing the decay rate (see below). It is therefore obvious that the bands with λ_{max}(1112-Tetra) = 450 nm and λ_{max}(1122-Tetra) = 430 nm must be due to the corresponding anion T^- with e^-_{solv} as their precursor.

B. Initial Kinetic Observations. A typical rate curve ($t^{-0.6}$ plot) for 0.2 M 1112-Tetra in MCH at 143 K is shown in Figure 2. The general shape is similar to the one found for chloroform[8] in MCH. The early part (large $t^{-0.6}$ values) again appears to correspond to the cationic mechanism ($M^{+*} \rightarrow MCH^+$, $MCHene^+$). The late part (small $t^{-0.6}$ values) reveals that the anion decay is much slower than that for chloroform. Therefore, the positive (early) and negative (late) processes are better separated in time than in the system with $CHCl_3$.

C. Initial Simulations. As usual, simulation has to start at late times, with the slower process (anion fragmentation with k^-) and then continue to early times (M^{+*} decay with k_{tot}).

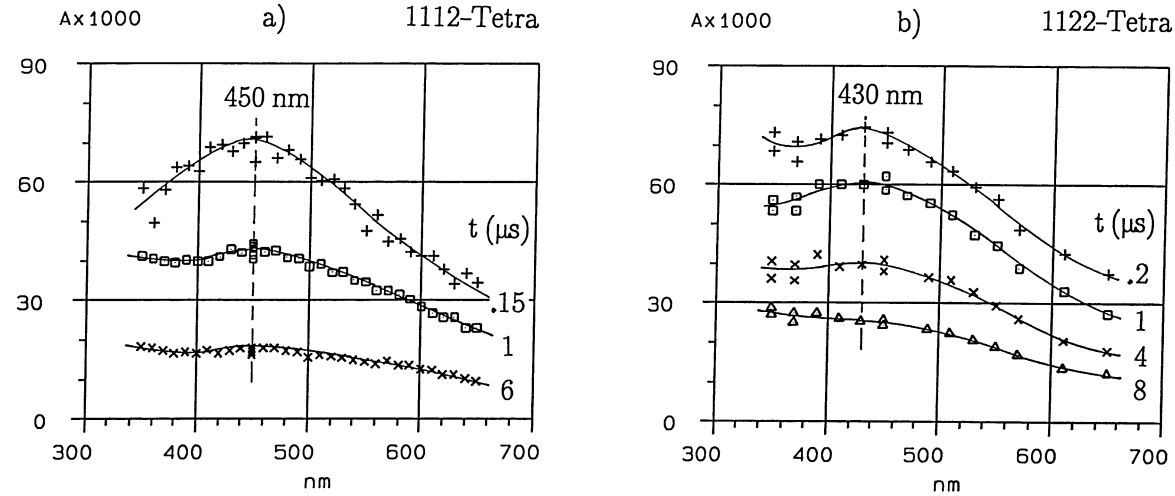

Figure 1. Transient spectra for the two isomers of Tetra in MCH at 143 K: (a) 0.2 M 1112-Tetra (bandwidth hwhm = 6400 ± 200 cm^{-1}) and (b) 0.2 M 1122-Tetra (bandwidth hwhm = 7200 ± 300 cm^{-1}). Absorbance *A* normalized to 100 Gy.

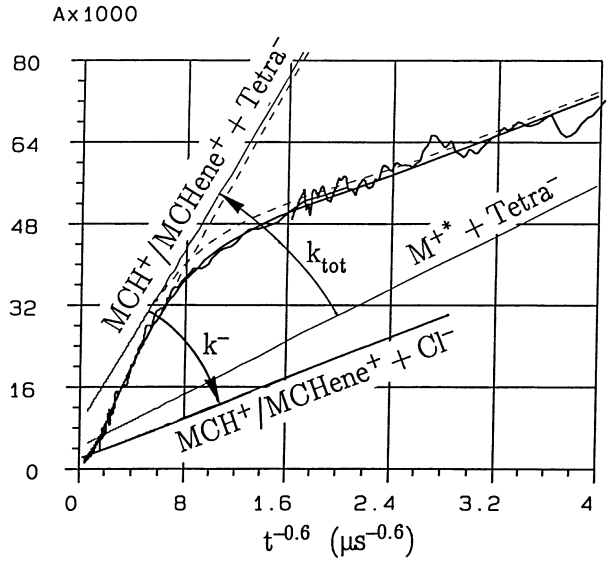

Figure 2. $t^{-0.6}$ plot of a rate curve at 450 nm for a solution of 0.2 M 1112-Tetra in MCH at 143 K. Absorbance *A* normalized to 100 Gy. The simulation corresponds to Scheme 1 and is based on the following data: the initial geminate pair (M^{+*}/$Tetra^-$) with $\alpha = 3.0\ \mu s^{0.6}$, IA = 4.3×10^{-3}; the primary mixed pair (MCH^+,$MCHene^+$/$Tetra^-$) with $\delta_{mix} = 5.0\ \mu s^{0.6}$, $ID_1 = 8.6 \times 10^{-3}$; the secondary mixed pair (MCH^+,-$MCHene^+$/Cl^-) with $\delta_{mix} = 5.0\ \mu s^{0.6}$, $ID_2 = 2.0 \times 10^{-3}$; and the two rate constants $k_{tot} = 1.6 \times 10^6\ s^{-1}$ and $k^- = 7.0 \times 10^4\ s^{-1}$.

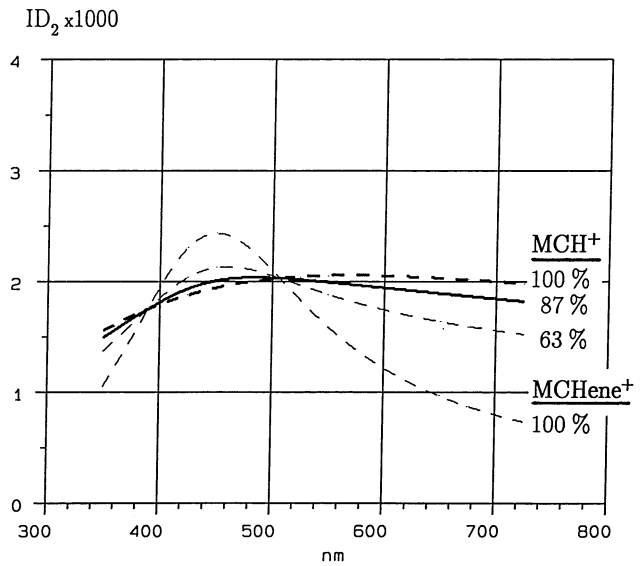

Figure 3. Calculated intercepts ID_2 for selected ratios of MCH^+ and $MCHene^+$ from the known spectra of MCH^+ and $MCHene^+$ alone,[8] with $G_{fi} = 0.06$ (100 eV)$^{-1}$. The curves for 87% and 100% MCH^+ correspond to δ_{mix} and δ_{fast}, respectively (see text). The curve for 63% MCH^+ is from the $CHCl_3$ system[8] for comparison.

The anion decay is so slow that the final $t^{-0.6}$ linearity (δ_2, ID_2) for the mixed geminate ions (MCH^+,$MCHene^+$/Cl^-) is not available. If the δ_2 values are taken from the $CHCl_3$ system,[8] then the resulting ID_2 values are too low, from what is known from previous experiments.[3,8,9,11] The ID_2 values (free ion yield) therefore were calculated from the known MCH^+ and $MCHene^+$ spectra[8] for the particular MCH^+/$MCHene^+$ ratio (Figure 3). The δ_2 values from the $CHCl_3$ system then were too large to simulate the systems with [T] < 0.1 M. δ_2 was reduced until a complete fit for all concentrations (5.3−530 mM Tetra) was reached (see Final Simulation).

Simulation of the early times revealed a very small concentration dependence for $k_{tot} = k_f + k_0 + k_2$[T]. Within error limits, k_2 appears to be near zero. In consequence, the δ_2 values should also be independent of [T]: there is no change of the ratio MCH^+/$MCHene^+$ with [T]. The mobility value δ_2 only depends on λ due to $\epsilon(MCH^+)$ and $\epsilon(MCHene^+)$ (see eq 6 of ref 1).

D. Final Simulations. *Several iterative cycles of simulations* were necessary to reach the above initial conclusions, using all experiments from system A (Table 1) covering the concentrations 5.3 mM ⩽ [T] ⩽ 530 mM. It was recognized that the rate constants k^- and k_{tot} varied rather little with the iteration cycles. The final experimental δ_2 value at 450 nm was $\delta_2 = 5.0\ \mu s^{0.6}$ (143 K). It corresponds to $k_r/k_f = 6.6$ (k_b/k_c in eq 6 of ref 1). This ratio allows us to calculate the λ dependence of δ_2 (Figure 4) and corresponds to a composition of about 13% $MCHene^+$ and 87% MCH^+ for the mixed cations. These δ_2 values represent upper limits for complete simulation. They will be called δ_{mix}. As δ_1 differs from δ_2 only by the mobility difference of the anion (T^- versus Cl^-), which is negligible relative to the high mobility of the cation, it is equal to δ_2, which means $\delta_1 = \delta_2 = \delta_{mix}$.

Alternative Simulation. For all data, the simulation is also possible with the lowest δ_2 value ($\delta_2 = 3.0$ at 143 K) corresponding to 100% MCH^+ yield (no M^{+*} fragmentation). This δ_2 represents the fastest process and will be called δ_{fast}. So far there are no clear criteria to decide about the real δ_2

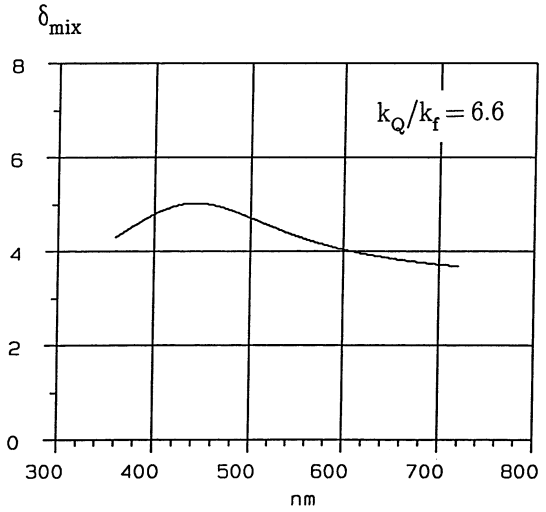

Figure 4. λ dependence of δ_{mix} as calculated from eq 6 in ref 1. It is based on the experimental value $\delta_{mix}(450\ nm) = 5.0\ \mu s^{0.6}$, which yields $k_r/k_f = 6.6$. The absorption coefficients of MCH^+ and $MCHene^+$, and the mobility values $\beta = 3.0\ \mu s^{0.6}$ for MCH^+ and $\gamma = 15.7\ \mu s^{0.6}$ for $MCHene^+$ are used as published.[8]

TABLE 2: Summary of the Rate Data at 143 K[a]

system	$k^-/10^4$ s^{-1}	$k_{tot}/10^6$ [b] s^{-1}
	1112-Tetra in MCH	
A, conc variation	(6.9 ± 1.0)	(1.70 ± 0.10)
B, λ variation	(8.0 ± 0.8)	(1.54 ± 0.14)
C, with N_2O sat.	(7.0 ± 0.8)	(1.61 ± 0.09)
mean	(7.3 ± 0.6)	(1.60 ± 0.10)[c]
	1122-Tetra in MCH	
G, temp variation	(5.0 ± 1.0)	(1.35 ± 0.20)

[a] On the basis of δ_{mix}. For the results with δ_{fast}, see the Discussion, part C. [b] $k_{tot} = k_f + k_0 + k_2[T]$. [c] As k_{tot} is not dependent on [T], $k_2 \approx 0$. With ~13% $MCHene^+$ (model with δ_{mix}) $k_f \approx 0.2 \times 10^6\ s^{-1}$ and $k_0 \approx 1.4 \times 10^6\ s^{-1}$.

between δ_{mix} (maximum) and δ_{fast} (minimum). All simulations have been done with both limiting values. However, if one looks back to all previous systems studied in MCH,[8,9,11] the fraction of $MCHene^+$ has always been higher than the 13%. It is expected that the results with δ_{mix} are the more likely ones. They are documented throughout in this paper. The kinetic results for δ_{fast} differ little from the ones with δ_{mix} and do not supply additional insights. For a comparison, see the Discussion, part C.

A typical simulation with δ_{mix} for a rate curve at 450 nm is seen in Figure 2 for 0.2 M 1112-Tetra at 143 K, corresponding to Scheme 1. The parameters for the three geminate pairs of ions and the rate constants for k_{tot} and k^- are given in the caption of Figure 2. The α value for the high mobility of M^{+*} was assumed to be identical to the one of MCH^+.[9] For a better value, see the Discussion, part B.

E. Dependence on Concentration [T]. From the kinetic analysis of all rate curves of system A with 1112-Tetra (Table 1) the concentration dependences of the rate constants k_{tot} and k^- and the intercepts (IA, ID_1) were derived with δ_{mix} (Figure 4).

The rate constant k^- for the anion fragmentation is constant within experimental error for the complete concentration range from 5.3 to 530 mM Tetra. This mean value for system A is $\overline{k^-} = (6.9 \pm 1.0) \times 10^4\ s^{-1}$ at 143 K (Table 2).

The rate constant k_{tot} is shown in Figure 5. Above the concentration of ~50 mM Tetra, k_{tot} is about constant, which means that k_2 must be near zero and $k_r \approx k_0$. Even if 0.2 M Tetra is saturated with N_2O (0.118 M), there is no further change of k_{tot} (see below: results with N_2O). The initial increase at very low [T] most likely is not real, as the accuracy rapidly drops at low [T]. k_{tot} at 570 nm (versus 450 nm) is expected to be more reliable (less interference from the strong anion absorption) and furthermore corresponds to the results from systems B and C (see Table 2). For system A the mean value is $\overline{k_{tot}} = (1.70 \pm 0.10) \times 10^6\ s^{-1}$, almost independent of [T] (Table 2). As δ_{mix} represents a yield of about 13% $MCHene^+$, the individual rate constants for fragmentation and relaxation (or isomerization) are $k_f \approx 0.2 \times 10^6\ s^{-1}$ and $k_r \approx 1.5 \times 10^6\ s^{-1}$.

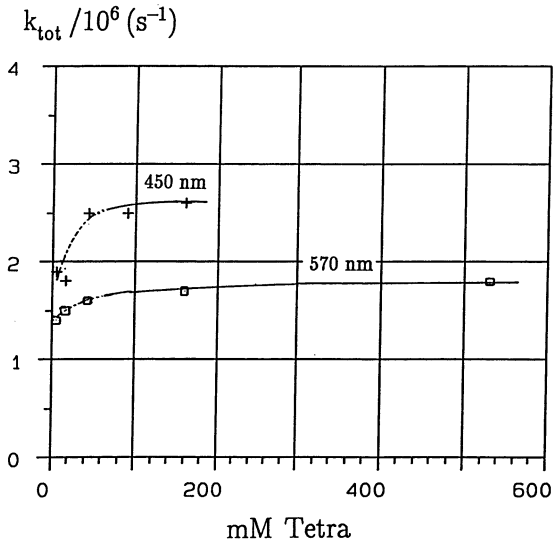

Figure 5. Concentration dependence of $k_{tot} = k_f + k_r$ with $k_r = k_0 + k_2[T]$ from the chemical system A (Table 1). For [T] $\gtrsim$ 50 mM the rate constant k_{tot} levels off, which means $k_2 \approx 0$ and $k_r = k_0$.

The free ion intercepts $IA(M^{+*}/Tetra^-)$ and $ID_1(MCH^+, MCHene^+/Tetra^-)$ are shown in Figure 6 (solid lines) as a function of [T]. The difference of $ID_1(MCH^+,MCHene^+/Tetra^-)$ and $ID_2(MCH^+,MCHene^+/Cl^-)$ corresponds to the absorption of $Tetra^-$, the expected free ion yield: $\Delta T^- = ID_1 - ID_{2,calc}$ (Figure 6b, heavy lines). All free ion intercepts (IA, ID_1, and ΔT^-) are increasing with [T]. They should, however, be constant, as soon as all free ions are scavenged by Tetra. This condition is met in the whole concentration range studied. For an explanation, see the Discussion, part A.

F. Free Ion Spectra. From system B (Table 1) with 0.2 M 1112-Tetra at 143 K, the intercept spectra for $IA(M^{+*}/T^-)$, $ID_1(MCH^+,MCHene^+/T^-)$, and $\Delta T^- = ID_1 - ID_2$ are shown in Figure 7. They are all dominated by the spectrum of $Tetra^-$ ($\lambda_{max} = 450$ nm). The intercept IA should correspond to the sum of the M^{+*} and $Tetra^-$ free ion yields. Therefore, IA should be larger than ΔT^-. This is clearly not the case. For an explanation, see the Discussion, part B. The rate constants k^- and k_{tot} are independent of λ. The mean values are given in Table 2.

G. N_2O as Additional Electron Scavenger. The rate analysis of a N_2O saturated solution of 0.2 M 1112-Tetra (system C, Table 1) confirms the initial observation that the 450 nm band is reduced uniformly by N_2O. The rate constants k^- and k_{tot}, however, remain, within error limits, identical to the results in system A and B (see Table 2). This is proof, that e_{solv} is the precursor to the 450 nm band and the band itself must be assigned to $Tetra^-$. N_2O is not affecting k_{tot} and therefore further confirms that the M^{+*} decay to MCH^+ and $MCHene^+$ is not affected by the solutes such as Tetra and N_2O (Table 2).

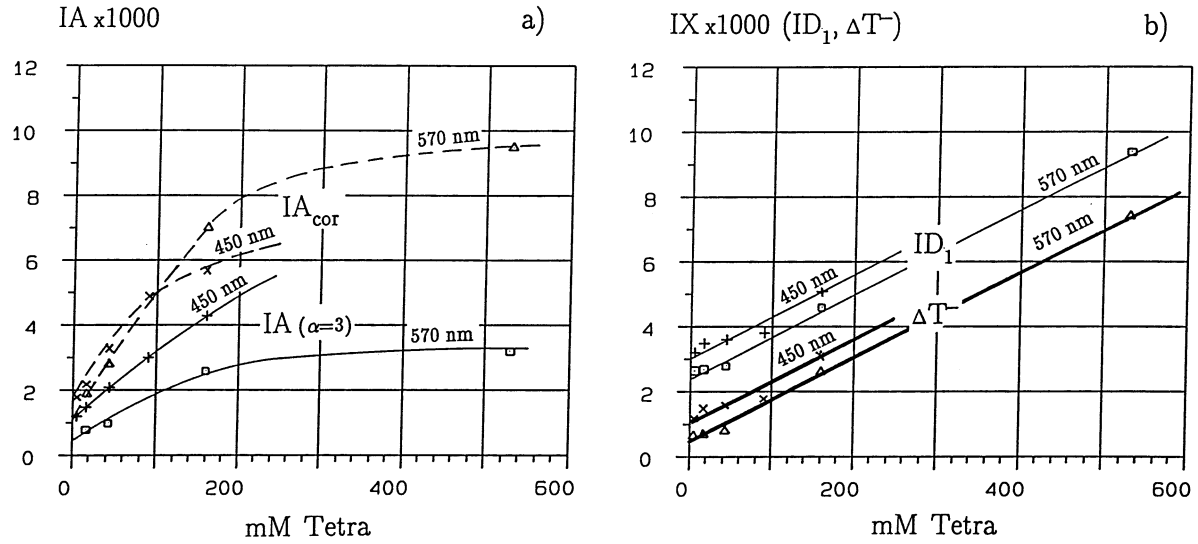

Figure 6. Concentration dependence of the free ion intercepts from the chemical system A (Table 1), normalized to 100 Gy. (a) IA(M^{+*},T^-) as determined for $\alpha = 3.0$ (assumed the mobility for M^{+*} to be identical to that for MCH^+). IA_{cor} (dashed lines), corrected for the higher mobility of M^{+*}: ~9 times faster than that of MCH^+ (see Discussion, part B). (b) ID_1(MCH^+,$MCHene^+$/T^-) and $\Delta T^- = ID_1 - ID_{2,calc}$. The latter represents the T^- yield in Scheme 1 or the T_2^- yield in Scheme 2 (see Discussion, part A).

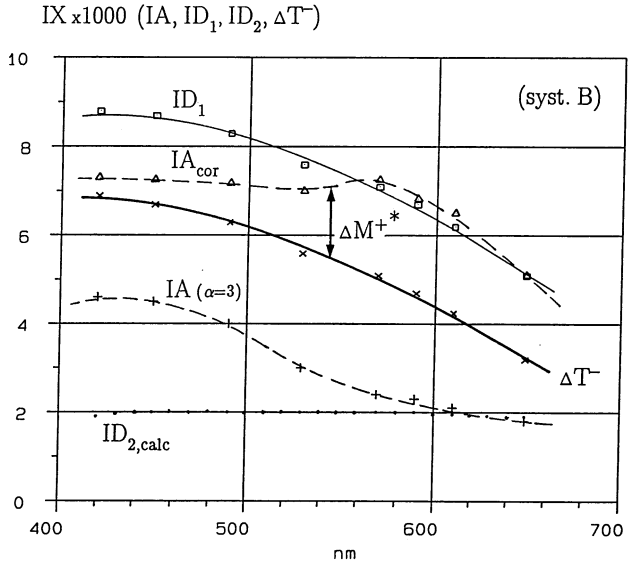

Figure 7. Free ion intercept spectra (chemical system B, Table 1), normalized to 100 Gy: IA(M^{+*}/T^-) as determined for $\alpha = 3.0$ (same mobility as that of MCH^+), ID_1(MCH^+,$MCHene^+$/T^-), $ID_{2,calc}$(MCH^+, $MCHene^+$/Cl^-), and $\Delta T^- = ID_1 - ID_2$. IA_{cor} is a corrected IA for the higher mobility of M^{+*} to ascertain that $IA_{cor} = \Delta T^- + \Delta M^{+*}$. ΔM^{+*} is the free ion contribution of M^{+*} (for details see Discussion, part B).

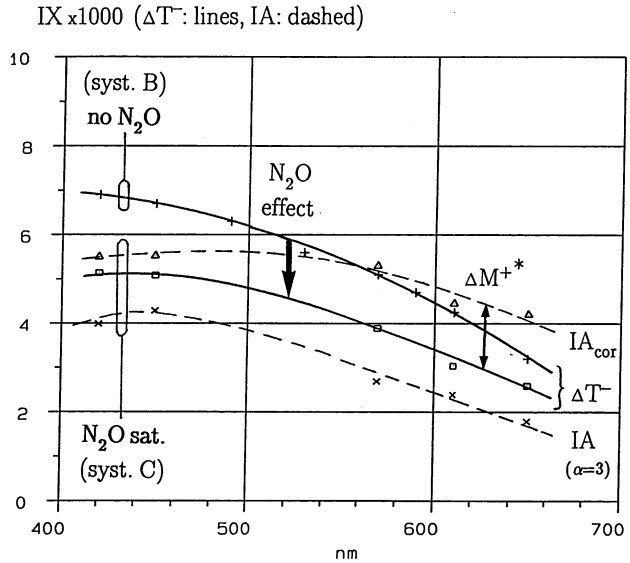

Figure 8. Effect of N_2O on the free ion intercept spectra (chemical system C versus system B, Table 1), particularly on $\Delta T^- = ID_1 - ID_2$. ΔT^- is reduced by 24 ± 3%. For IA ($\alpha = 3$) and IA_{cor}, see the caption of Figure 7 and the Discussion, part B.

The free ion yield of $Tetra^-$ ($\Delta T^- = ID_1 - ID_2$) is reduced with N_2O by 24 ± 3% (comparison of ΔT^- for systems B and C in Figure 8). This is again support for e_{solv} being the precursor to the 450 nm band (assigned to $Tetra^-$).

The initial IA(M^{+*}/T^-) for $\alpha = 3.0$ (143 K) is again smaller than ΔT^-, a discrepancy which will be treated in the Discussion, part B.

H. Temperature Dependence of the Kinetic Parameters. The effect was studied for both Tetra isomers at 450 nm: system D for 1112-Tetra and system G for 1122-Tetra (Table 1). The mobility values α (for MCH^+) and δ_{mix} (for MCH^+, $MCHene^+$), used for the kinetic analysis, are listed in Table 4. From the rate curve simulations, the temperature dependences of k^- and k_{tot}, as well as of the intercepts IA, ID_1, and $\Delta T^- = ID_1 - ID_2$ were derived.

The Arrhenius plots for the rate constants are shown in Figure 9, and the corresponding data are summarized in Table 3. For k^- above ~163 K there is a beginning deviation from linearity. The attached anion equilibrium (eq 12) is so fast that it is not expected to be the origin of the deviation (see the Discussion, part A). Log *A* for the anion decay is about 11. This again excludes the possibility that the 450 nm band would be due to a solvent separated ion pair as for CCl_4[2,15] or hexachloroethane[1] in MCH. Its decay would ask for log *A* to be about 9−10.[15,16]

It is surprising that the free ion yield of $Tetra^-$, derived from $\Delta T^- = ID_1 - ID_2$, is extremely temperature dependent for both isomers (Table 4). The G_{fi} values vary by a factor of 2 only from 133 to 295 K (150 K difference),[3] whereas ΔT^- for 1112-Tetra varies by a factor of 8 over just 30 K (133 to 163 K). This needs an explanation: see the Discussion, part A.

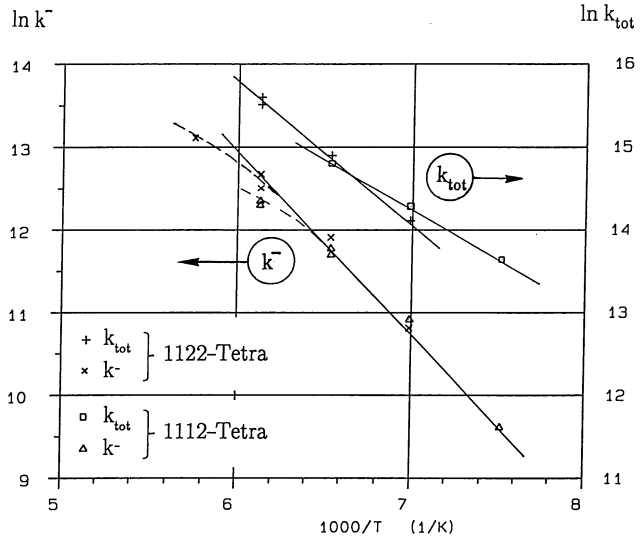

Figure 9. Arrhenius plots for the rate constants k^- and k_{tot} for the two isomers 1112-Tetra and 1122-Tetra (chemical systems D and G, Table 1). For the Arrhenius parameters see Table 3.

TABLE 3: Arrhenius Parameters for the Rate Data (δ_{mix} Model)

	1112-Tetra (syst D)	1122-Tetra (syst G)
temp range	133−153 K	143−163 K
k^-	$E_{act} = 17.8$ kJ/mol	$E_{act} = 16.9$ kJ/mol
	$\log A = 11.19$	$\log A = 10.9$
	$r = 0.9966$	$r = 0.9915$
k_{tot}	$E_{act} = 9.83$ kJ/mol	$E_{act} = 13.9$ kJ/mol
	$\log A = 9.79$	$\log A = 11.2$
	$r = 0.99994$	$r = 0.9983$

TABLE 4: Temperature Dependence of the Mobility Values α and δ_{mix} as Used in Simulation and of the Experimental "Free Ion Yields" ΔT^- at 450 nm

temp K	α[a] at all λ $\mu s^{0.6}$	δ_{mix}[b] at 450 nm $\mu s^{0.6}$	$\Delta T^- \times 10^3$ (from $ID_1 - ID_2$) 1112-Tetra (syst D)	1122-Tetra (syst G)
133	4.5	7.5	8.2	
143	3.0	5.0◊	4.0	11.2
153	2.0	3.3	2.8	8.5
163	1.5	2.5	1.1	5.9
173	1.14	1.9		4.0
183	0.88	1.5		2.6

[a] The mobility value for MCH^+.[8] [b] δ_{mix} assumed to be proportional to α with ◊ as the experimental reference value (α is a relevant guideline, since the MCH^+ yield is about 87%).

V. Discussion

A. Concentration Dependence of the Free Ion Intercepts: The Anion Equilibrium $T^- + T \rightleftharpoons T_2^-$. The intercepts are the sum of the free ion absorptions: for IA from M^{+*} and T^-, for ID_1 from the mixed cations $MCH^+/MCHene^+$ and T^-, and for $\Delta T^- = ID_1 - ID_2$ from T^- alone. In all intercepts (except ID_2), T^- is involved.

To ensure that the free ion yield of T^- is constant, scavenging of e^-_{solv} by T must be completed, before the free ion recombination sets in. At 143 K this is at $t^{-0.6} \approx 0.15\ \mu s^{-0.6}$.[3] Therefore, the anchor point AP (ref 14) for $e^-_{solv} + T$ must be higher than $0.15\ \mu s^{-0.6}$. With $k_e = 4.8 \times 10^8\ M^{-1}\ s^{-1}$ (see Results), this condition means [T] > 0.5 mM. As our lowest concentration of T is 10 times higher, all free ion intercepts should be constant throughout the complete [T] range. This is clearly not the case (Figure 6) and is beyond experimental error limits.

Theoretically, such an increase of intercepts with [T] could be explained by referring to an ion recombination leading to a product absorber. Equation 10 in ref 1 shows that in this case the intercept depends on G_{tot} (total scavenging yield), which obviously is dependent on the scavenger concentration [T]. However, it has previously been shown[1] that such a model with large intercepts is not able to simulate the rate curves from the Tetra system.

It remains to consider *the formation of dimer anions* T_2^- *through an equilibrium*

$$T^- + T \underset{k^{\leftarrow}}{\overset{k^{\rightarrow}}{\rightleftharpoons}} T_2^-$$

with T_2^- being the absorber at 450 nm (not T^-). With increased [T] the equilibrium will be shifted toward T_2^- and the corresponding intercept (now due to T_2^-) will increase, in agreement with the experiment (Figure 6).

The kinetics introduced by such an equilibrium is represented by Scheme 2 (Scheme 1 modified for the anion mechanism). The buildup rate for this first-order system is $k_{up} = k^{\rightarrow}[T] + k^{\leftarrow}$. So far only electron scavenging had to be completed for the anionic buildup. Now, further delay for the 450 nm absorber (T_2^-) occurs through k_{up}. For this purpose the rate constants $k^{\rightarrow}$ and $k^{\leftarrow}$ must be evaluated.

The forward rate constant $k^{\rightarrow}$ is calculated from the diffusion constants $D(Tetra) \approx D(Tetra^-) \approx 10^{-8}\ cm^2\ s^{-1}$ (see Results). With reactant radii of 0.3 nm, this leads to $k^{\rightarrow}(143\ K) = 10^7\ M^{-1}\ s^{-1}$.

The backward rate constant $k^{\leftarrow}$ is less obvious. It may be estimated from three conditions it has to meet, not to interfere with the experimental findings:

(a) The equilibrium buildup (being [T] dependent) should not interfere with the time range in which k^- is determined, as k^- is not [T] dependent. This means that AP_{up} (the anchor point[14] for the buildup process) should be higher than the starting point for k^- matching: $AP_{up} > 0.7$. This means $k_{up} > 2.5 \times 10^6\ s^{-1}$, and $k^{\leftarrow} > 2.4 \times 10^6\ s^{-1}$ from the lowest [T].

(b) Similarily, k_{tot} is independent of [T] for [T] $\gtrsim$ 50 mM and should therefore not be disturbed by k_{up} in the range $AP_{tot} < t^{-0.6} \lesssim AP_{tot} + 0.6$, the range which is needed for the k_{tot} determination. With $AP_{tot} = 0.53$ the condition is $AP_{up} > 1.2$. This means $k_{up} > 6.2 \times 10^6\ s^{-1}$, and $k^{\leftarrow} > 5.7 \times 10^6\ s^{-1}$ for 50 mM Tetra.

(c) Simulation in the early stage ($1.2 < t^{-0.6} < 4\ \mu s^{-0.6}$) defines the intercept IA for α = 3. If the equilibrium buildup (with AP_{up}) would reach into this $t^{-0.6}$ range, the rate curve would further deviate toward earlier times and a single parameter IA would not be able to simulate the early stage. The condition for this early stage therefore is $AP_{up}(10\%) \gtrsim 3.0\ \mu s^{-0.6}$ (ref 14) (10% rest of buildup reaction due to larger noise level in this early time). This yields $k_{up} > 1.5 \times 10^7\ s^{-1}$ and therefore $k^{\leftarrow} \gtrsim 1.5 \times 10^7\ s^{-1}$ for the lowest [T].

Condition c obviously is the most stringent one. In fact, the equilibration is very fast: $\tau_{up} < 66$ ns. It is therefore not possible to distinguish whether fragmentation occurs from the monomer or dimer anion, from T^- or T_2^-, or from both. The equilibrium rate data also reveal that the T_2^- yield is less than half of the total free ion yield (for the [T] range studied: chemical system A). This finds support in Figure 6b, where ΔT^- (T_2^- yield) is about linear up to 530 mM Tetra (not yet leveling off).

It is concluded that Scheme 2 with the equilibrium $T^- + T \rightleftharpoons T_2^-$ is able to reproduce the facts. This also explains the strong temperature dependence of $\Delta T^- = ID_1 - ID_2$ (Table 4),

as ΔT^- now is due to T_2^- and the temperature effect is through the equilibrium. It is expected that the absorption band for T_2^- at 450 nm corresponds to a charge resonance band ($T \leftarrow T^-$). The relatively large bandwidth (Figure 1) might be support for that assignment.

B. Precursor M^{+*} and Its Mobility. In Figure 7 the intercept spectrum for IA(α=3), due to the free ion yields of M^{+*} and T^-, was found to be smaller than ΔT^- for T^- alone (T^- now should be replaced by T_2^-; see previous paragraph). IA has to be larger than ΔT^- by the free ion contribution of M^{+*} (here called ΔM^{+*}). One should remember that, originally,[9] the mobility of M^{+*}, with a lack of any criteria, was assumed to be identical to the mobility of MCH^+: $\alpha(M^{+*}) = \alpha(MCH^+) = 3.0\ \mu s^{0.6}$ at 143 K. This allowed us to derive an absolute spectrum $\epsilon(M^{+*})$ from the intercept spectrum of M^{+*}.[9] These $\epsilon(M^{+*})$ values now appear to be too low. To increase IA to a value larger than ΔT^-, the α value must be lowered, which means the mobility of M^{+*} must be higher than that for MCH^+.

The amount of lowering α *was determined by the following iteration:* The initial IA was set to $IA_1 = \Delta T^-_{exp} + \Delta M^{+*}$ (from ref 9 with $\alpha_0 = 3.0$). With this new IA, a new, lower α had to be derived by simulation of the experimental rate curve at early times ($2 \leqslant t^{-0.6} \leqslant 4\ \mu s^{-0.6}$). The new α initiates a higher contribution of ΔM^{+*}.[9] For the *i* step of the iteration, $IA_i = \Delta T^-_{exp} + \Delta M^{+*}(\alpha_{i-1})$ and the simulation again yields a new α_i. The iteration ends when α_i does not alter any more.

The final α *is called* α_{cor}. *The corrected intercepts* IA_{cor} are shown in Figure 7 and in Figure 6a. The area in Figure 7 between IA_{cor} and ΔT^- corresponds to the final ΔM^{+*} contribution. Unexpectedly, the values for α_{cor} systematically vary with λ with a maximum at 450 nm ($\alpha_{cor} = 1.7$) and a minimum around 600 nm ($\alpha_{cor} = 0.8$). As the effect is systematic, quoting an average value is not reasonable. From a detailed search for the origin of this puzzling λ dependence, it became rather firm that the difficulty relates to the accuracy with which ΔT^- was determined from the intercept differences ($ID_1 - ID_2$). In the range $570 < \lambda < 650$ nm the values for α_{cor} are almost independent, whether $\Delta T^- = ID_1 - ID_2$ values were determined with δ_{mix} or δ_{fast} (see the Discussion, part C). It is concluded that the data in this λ range are more reliable: $\overline{\alpha_{cor}} = 0.83 \pm 0.05\ \mu s^{0.6}$. Due to eq 1 the corresponding M^{+*} mobility, $D(M^{+*})$, is about 9 times higher than that for MCH^+. The M^{+*} free ion spectrum ($\epsilon(M^{+*})$) must be about 3 times larger than that previously published.[9]

Due to the anion equilibrium $T^- + T \rightleftharpoons T_2^-$ introduced in the previous paragraph, the experimental ΔT^- value (T_2^- absorption) does not represent the total free anion yield. With a correction to 100% anion yield, α_{cor} would be even lower and the mobility of M^{+*} higher than 9 times the mobility of MCH^+, and $\epsilon(M^{+*})$ would increase by more than 3 times over the published value.[9] Due to these unknown corrections, one should not derive absolute values for $D(M^{+*})$ and $\epsilon(M^{+*})$.

For the N_2O *saturated 0.2 M Tetra solution* (chemical system C), Figure 8 shows again that IA is smaller than ΔT^- and therefore again needs a correction to higher mobility of M^{+*} with a lower α_{cor}. The corrected IA_{cor} is shown in Figure 8. From the λ range 570−650 nm, $\overline{\alpha_{cor}} = 1.32 \pm 0.19$ is higher than that for the system without N_2O. This reflects the fact that ΔT^- (T_2^- absorption) not only is lower due to the anion equilibrium, $T^- + T \rightleftharpoons T_2^-$, but also is due to N_2O scavenging (by −24%). These results from system C are quite compatible with the proposal of higher mobility for M^{+*}.

Previously, the effect of N_2O (ref 9) or $CHCl_3$ (ref 8) was compared with a quenching effect on M^{+*}, as the solute affected the yield of relaxed MCH^+ relative to the fragment cation $MCHene^+$. In the MCH solution of Tetra, this is not the case (no [T] dependence of k_{tot}). This indicates that the star (*) in M^{+*} rather signals a state of higher energy (or of higher ionization potential), in agreement with the conclusions in the paper on quadricyclane in MCH.[11]

C. Comment. It has been suggested that the model with δ_{mix} (mixed cation pair with 13% $MCHene^+$ and 87% MCH^+) is more likely than the model with δ_{fast} (MCH^+ as the only product cation). In this paper all results therefore are given for δ_{mix} (Figure 4). However, it cannot be excluded that the real δ value is somwhere between δ_{mix} and δ_{fast}. This comment summarizes the effect on the results, if, in the extreme case, $\delta_{real} = \delta_{fast}$.

The anion lifetime (k^-) would not change. *The rate constant* k_{tot} is about 10% larger but still not dependent on [T] ($k_2 = 0$). *The Arrhenius plots for* k^- *and* k_{tot} for both isomers are parallel and very close to the curves in Figure 9. For k^-, E_{act} is smaller by 4−10% and log A by 2−6%. For k_{tot}, E_{act} is smaller by 4−14% and log A by 1−4% (first number is for 1122-Tetra, second for 1112-Tetra). *The intercepts* ID_1 (MCH^+/T_2^-) and ΔT^- (yield of T_2^-) are about two times larger (because δ is lower) with the same concentration dependence as those in Figures 6b, 7, and 8. *The derived* α_{cor} *values* (see the Discussion, part B) are about 17% lower, which means that the stated mobility minimum for M^{+*} would be about 36% larger (means at least 12 times the mobility of MCH^+). The conclusion in the previous paragraph (Discussion, part B) remains valid: the M^{+*} mobility is at least 9 times higher than the one for MCH^+.

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(14) Due to time compression toward late times in $t^{-0.6}$ plots, the "end" of a reaction corresponds to an easily recognizable point, called the "anchor point" (AP) for the particular reaction.[13] It is usually calculated for 99% completion of the reaction (1% rest) by $AP = x(k_1 \times 10^{-6})^{0.6}\ \mu s^{-0.6}$ with $x = 0.4$. For 5% rest, AP(5%) has $x \approx 0.5$, and for 10% rest, AP(10%) has $x \approx 0.6$.
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