Kinetic Studies Concerning the Decay of Nitronic Acids in Polymer Matrices Using a Data Evaluation Method Based on Dispersive Kinetics

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ABSTRACT: Evaluation methods based on *dispersive kinetics* were applied to derive kinetic parameters for the rearrangement of differently α-substituted nitronic acids generated by flash photolysis (λ_{inc} = 347 nm) of *o*-nitrobenzyl esters. The rearrangements were performed in polymer matrices of different chemical nature: poly(methyl acrylate) (PMA), poly(methyl methacrylate) (PMMA), poly(styrene) (PSt), and poly(dimethylsiloxane) (PDMS). A nonexponential decay behavior was observed in rigid and highly viscous matrices which can be characterized by the average rate constant $\bar{\nu}$ and the dispersion factor σ. It was found that the apparent activation energy of the average rate constant of the unimolecular reaction is inherent to the nitronic acid and depends, if at all, only slightly on the chemical nature of the matrix and on the mobility of the matrix. However, the mobility of the matrix exerts a strong influence on the dispersion factor σ which is a measure of the width of the Gaussian distribution of individual energy barrier heights. σ decreases with increasing temperature but approaches zero (transit from dispersive to nondispersive, i.e., first-order kinetics) at temperatures definitely higher than T_g. The more pronounced this effect is, the bulkier is the substituent at the α-position of the nitronic acid. The activation entropy ΔS^* was found to be negative in all cases, thus substantiating the existence of a formerly postulated cyclic intermediate. ΔS^* depends only slightly on the chemical nature of the matrix but significantly depends on the chemical nature of the nitronic acid: in the case of the unsubstituted nitronic acid, ΔS^* is much lower than in the cases of the substituted ones. This difference is thought to be due to hydrogen bonding which is only feasible in the case of the unsubstituted compound.

1. Introduction

Recently, thermally induced intramolecular rearrangement and isomerization reactions of various compounds in polymeric matrices have attracted the interest of several research groups.[1-13] A kinetic feature common to these processes is that first-order kinetics do not apply over a broad temperature range. Relevant investigations have been performed, e.g., with merocyanine compounds[3,10-12] and azo compounds.[4-6] Our own contribution to this field pertains to the decay of nitronic acids.[13] The latter can be generated by UV irradiation (e.g., at λ = 347 nm) of *o*-nitrobenzyl esters as depicted in Scheme 1. Compared to the formation rate, which is quite fast (τ_f < 1 ns), the decay rate of nitronic acids is rather slow: in fluid solutions τ_d ranges from microseconds to milliseconds, depending on the chemical nature of the substituents R^1 and R^2 and on the chemical nature and the mobility of the surrounding matrix. Therefore, the decay of nitronic acids can be conveniently studied by 20-ns flash photolysis. Upon studying copolymers of methacrylate or acrylate containing 5 mol % *o*-nitro-α-methylbenzyl acrylate,[13] it turned out that the decay of nitronic acid was nonexponential even at temperatures extending significantly beyond the glass transition temperature. The present paper reports on the continuation of this research. Contrary to the former work dealing with polymers containing *o*-nitrobenzyl groups chemically attached to the polymer backbone, this work concerns polymer matrices containing physically admixed *o*-nitrobenzyl benzoates and isobutyrates (see Table 1). It was aimed at finding out how the decay kinetics depend (a) on the chemical nature of the substituent in the α-position in the *o*-nitrobenzyl ester and (b) on the chemical nature of the matrix. For this reason poly(methyl methacrylate), poly(methyl acrylate), poly(styrene), and poly(dimethylsiloxane) were used as polymer matrices (see Table 2).

Scheme 1. Mechanism of the Photorearrangement of *o*-Nitrobenzyl Esters

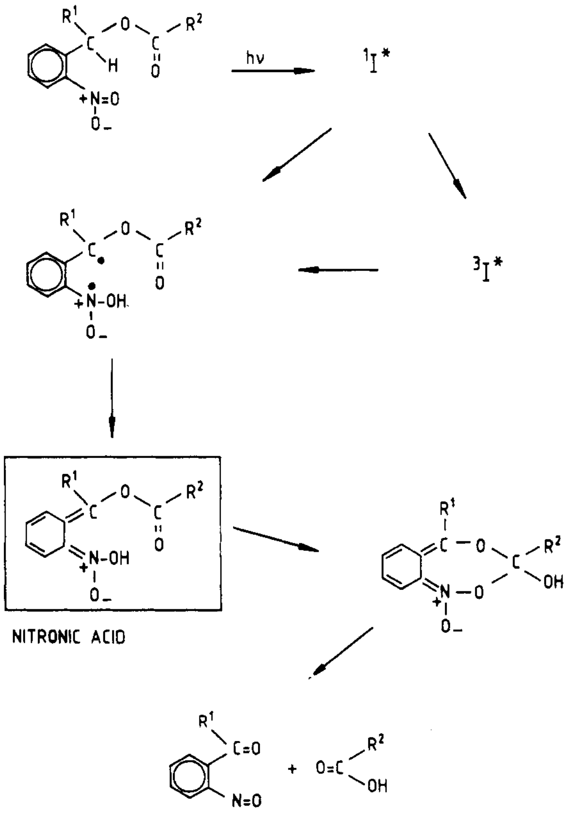

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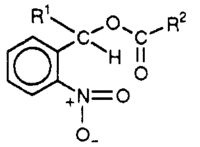
Table 1. o-Nitrobenzyl Benzoates and Isobutyrates



denotation	R^1 [a]	R^2 [a]	$\epsilon_{347\ nm}$ (L mol^{-1} cm^{-1})
o-nitrobenzyl benzoate (oNBB)	H	Ph	290 ± 10[b]
α-methyl-o-nitrobenzyl benzoate (αMoNBB)	CH_3	Ph	375 ± 10[b]
α-phenyl-o-nitrobenzyl benzoate (αPoNBB)	Ph	Ph	346 ± 10[b]
o-nitrobenzyl isobutyrate (oNBIB)	H	$CH(CH_3)_2$	232 ± 10[c]
α-methyl-o-nitrobenzyl isobutyrate (αMoNBIB)	CH_3	$CH(CH_3)_2$	268 ± 10[c]
α-phenyl-o-nitrobenzyl isobutyrate (αPoNBIB)	Ph	$CH(CH_3)_2$	253 ± 10[c]

[a] Ph = phenyl. [b] Measured in CH_3CN solution at room temperature. [c] Measured in poly(dimethylsiloxane) solution at room temperature.

2. Experimental Part

2.1. Materials. The unsubstituted and the α-substituted o-nitrobenzyl benzoates and isobutyrates listed in Table 1 were obtained from BASF AG and used without further purification. Poly(methyl methacrylate) (PMMA) and poly(styrene) (PSt) were prepared by free-radical polymerization of methyl methacrylate and styrene, respectively, using azobis(isobutyronitrile) (AIBN) as initiator. The polymers were purified by repeated precipitation from an acetone solution with methanol (PMMA) and from a toluene solution with ethanol (PSt). Poly(methyl acrylate) (PMA) was prepared by irradiating an acetone solution of methyl acrylate (38 vol %) with γ-rays. After irradiation, the polymer was precipitated with methanol and three times reprecipitated from an acetone solution with methanol. Molar masses of PMMA, PMA, and PSt were determined by GPC using commercial PMMA or PSt standards. The following glass transition temperatures were measured with the aid of a differential scanning calorimeter (Perkin-Elmer, Model DSC 2): 293 ± 2 K (PMA), 373 ± 2 K (PSt), and 378 ± 2 K (PMMA). Poly(dimethylsiloxane) (PDMS) was kindly provided by BAYER AG. The molar masses of the *Baysilon Oel* samples used in this work were determined by light scattering measurements: $M_w = 3.0 \times 10^4$ (M 1000) and $M_w = 8.4 \times 10^4$ (M 10 000).

2.2. Preparation of Films. The polymers were dissolved at room temperature during 24 h in a benzene solution of the o-nitrobenzyl benzoates. The concentrations were properly adjusted in order to obtain a final benzoate content in the film of 0.07 mol L^{-1}. Films were cast on quartz plates (Herasil, 75 × 15 × 1 mm) with the aid of a motorized film applicator (Erichson Model 509/1). After drying for 24 h at room temperature, they were gradually heated to a temperature $T = T_g + 20$ K during a period of 3 days in a vacuum oven at 0.1 Torr. The film thickness was 180 μm as determined by a digital micrometer (Svilupo Tecnologie Avanzate). For a given film the thickness varied by ±8 μm (controlled by optical absorption measurements).

2.3. Irradiation of o-Nitrobenzyl Esters in Polymer Films. Polymer films containing ca. 0.07 mol L^{-1} o-nitrobenzyl benzoate or isobutyrate were irradiated with single 20-ns flashes of 347-nm light generated by a ruby laser (Korad, Model K1 QS2) operated in conjunction with a frequency doubler. The irradiations were performed between 218 and 483 K in a cryostat (Oxford Instruments, Model DN 1704). After insertion of a sample plate, the cryostat was evacuated to 10^{-5}–10^{-6} Torr for a period of 3 h. Prior to irradiation it was filled with O_2-free argon. The plate could be moved up and down with the aid of a vacuum passage device (Balzers, rotary linear motion feed-through DN 40KF). In this way six different sections of each film could be irradiated. The change in optical density of the films was recorded as a function of time after the flash. For this purpose, the film was located in the cryostat in a manner allowing both the photolyzing and the analyzing light beams to be incident on the film at angles of 45°.

2.4. Irradiation of o-Nitrobenzyl Esters in Poly(dimethylsiloxane). o-Nitrobenzyl esters were dissolved in poly(dimethylsiloxane). The solutions were irradiated in rectangular quartz cells placed in a cryostat (Oxford Instruments). Prior to irradiation with 20 ns flashes of 347 nm light (vide ante section 2.3) the solutions were purged with purified argon.

2.5. Determination of the Rate of Decay of Nitronic Acids. Nitronic acids were formed during the 20-ns flash upon irradiation of oNBB, αMoNBB, or αPoNBB embedded in different polymer matrices (PMA, PMMA, PSt, and PDMS). The characteristic absorption bands of the three nitronic acids are located in the wavelength range between 400 and 450 nm.[17] In this work the rate of decay of the nitronic acids was measured by recording the change in the optical density at 400 nm (oNBB, αMoNBB, oNBIB, and αMoNBIB) or at 440 nm (αPoNBB and αPoNBIB).

3. Treatment of Kinetic Data

Figure 1 presents typical semilogarithmic plots of the decay of the nitronic acid. Plotted is the optical density, OD, which is proportional to the concentration of the nitronic acid, c, as a function of time. Obviously, in fluid solution, the decay follows first-order kinetics as indicated by the linear time dependence of $\ln(OD_t/OD_0)$, but in the rigid film it follows a nonexponential decay law. This kind of kinetic matrix effect is attributed to the existence of a distribution of "environments of varying quality" of the nitronic acid molecules which gives rise to a dispersion, i.e., a spectrum of individual rate constants. As has been pointed out by Kryszewski et al.,[3] the environmental effect can be related to the existence of a distribution of free volume elements (with respect to both size and location), giving rise to a dispersion of rotational diffusion constants.

In the most simple way nonexponential decay curves can be treated by applying Kohlrausch's empirical law:[16]

$$c_t/c_0 = \exp[-\alpha t^{\beta}] \qquad (1)$$

With $\alpha = \gamma^{\beta}$ eq 1 is transformed to eq 2:

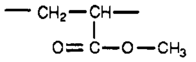
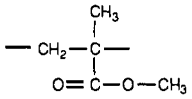
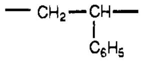
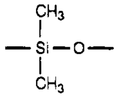
$$c_t/c_0 = \exp[-\gamma^{\beta} t^{\beta}] \qquad (2)$$

It will be shown below that γ has the quality of a rate constant and β is a measure of the extent of dispersion (dispersion factor). Equation 2 also can be written in the form:

$$\log[\ln(c_0/c_t)] = \beta \log \gamma + \beta \log t \qquad (3)$$

Consequently, γ and β can be obtained from plots of $\log[\ln(c_0/c_t)]$ vs $\log t$. According to quite a general approach of Siebrand et al.[14,15] which recently has been widely applied by Bässler et al.,[10–12] the dispersion arises from

Table 2. Polymers

denotation	formula of repeating unit	M_w	T_g (K)
poly(methyl acrylate) (PMA)	 $-CH_2-\underset{O=C-O-CH_3}{\underset{\vert}{CH}}-$	1.35×10^6	293[a]
poly(methyl methacrylate) (PMMA)	 $-CH_2-\overset{CH_3}{\overset{\vert}{\underset{O=C-O-CH_3}{\underset{\vert}{C}}}}-$	7.5×10^5	387[a]
poly(styrene) (PSt)	 $-CH_2-\underset{C_6H_5}{\underset{\vert}{CH}}-$	3.8×10^5	373[a]
poly(dimethylsiloxane) (PDMS)	 $-\overset{CH_3}{\overset{\vert}{\underset{CH_3}{\underset{\vert}{Si}}}}-O-$	3.0×10^4 8.4×10^4	153[18]

[a] Determined with films containing o-nitrobenzyl benzoate (0.07 mol L^{-1}).

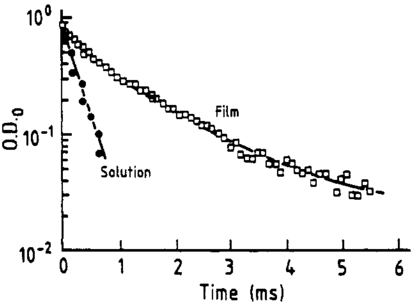


Figure 1. Decay of nitronic acid generated by photolysis of αMoNBB at 293 K in a rigid polymer matrix (PMA) and in a fluid solution (methyl isobutyrate). Typical first-order plots. [αMoNBB] = 0.07 mol L^{-1} (film) and 7×10^{-4} mol L^{-1} (fluid solution).

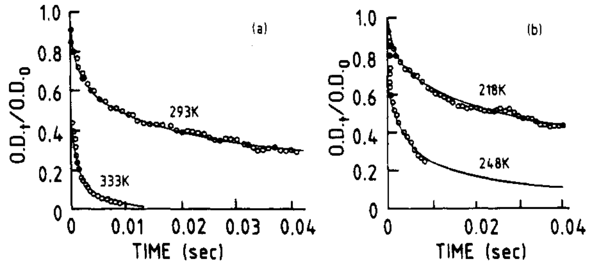


Figure 2. Plots of the normalized OD at λ_{obs} = 400 nm as a function of time. (a) oNBB in a PMMA matrix. (b) αMoNBB in a PMA matrix. Full lines were calculated with the aid of eq 4: (a) $\overline{\Delta\epsilon}$ = 53 kJ mol^{-1}, $\bar\nu$ = 54.6 s^{-1}, σ = 5.1 kJ mol^{-1} (293 K) and $\bar\nu$ = 665 s^{-1}, σ = 4.7 kJ mol^{-1} (333 K); (b) $\overline{\Delta\epsilon}$ = 30 kJ mol^{-1}, $\bar\nu$ = 22.2 s^{-1}, σ = 4.6 kJ mol^{-1} (218 K) and $\bar\nu$ = 446 s^{-1}, σ = 4.7 kJ mol^{-1} (248 K).

random variations of the energy barrier controlling molecular motions. It is postulated that the individual decay rate constants are thermally activated and that the individual energy barrier heights $\Delta\epsilon$ are subject to a Gaussian distribution around a mean value $\overline{\Delta\epsilon}$ with a standard deviation σ. The data treatment according to the model proposed by Siebrand et al.[14,15] is based on the following integral equation:

$$c_t/c_0 = \int_{-\infty}^{\infty} h(\Delta\epsilon)\exp[-\nu(\Delta\epsilon)\,t]\,d(\Delta\epsilon) \qquad (4)$$

Here, $\nu(\Delta\epsilon) = \nu_0 \exp[-\Delta\epsilon/RT]$ is the rate constant of an individual elementary reaction with the activation energy $\Delta\epsilon$ and $h(\Delta\epsilon)$ is the distribution function of the activation energy. In a polymer matrix $\Delta\epsilon$ is thought to depend on various conformational parameters which are subject to statistical variations. Therefore, it seems reasonable to consider the activation energy to be Gaussian:

$$h(\Delta\epsilon) = \frac{1}{(2\pi\sigma^2)^{1/2}}\exp[-(\Delta\epsilon - \overline{\Delta\epsilon})^2/2\sigma^2] \qquad (5)$$

Here, σ denotes the dispersion factor and $\overline{\Delta\epsilon}$ the mean activation energy of the thermally activated decay of the nitronic acid in a polymer matrix. Upon fitting the measured time dependence of c_t/c_0 to eq 4, two independent parameters are obtained, the dispersion factor σ and the average rate constant $\bar\nu$ given by eq 6:

$$\bar\nu = \nu_0 \exp[-\overline{\Delta\epsilon}/RT] \qquad (6)$$

The mathematical treatment applied in the present work to determine $\bar\nu$ and σ is based on finding the global minimum of the expression

$$\sum_{i=1}^{N}\{c(t_i;\bar\nu,\sigma)/c(t_0) - c_{exp}(t_i)/c_{exp}(t_0)\}^2$$

Here, N is the number of experimental points. $c_{exp}(t_i)/c_{exp}(t_0)$ denotes the experimental values at time t_i normalized with respect to the initial value and $c(t_i;\bar\nu,\sigma)/c(t_0)$ the theoretical values calculated according to eq 4.

This was achieved by a numerical procedure using the "gradient method". Upon calculating the integral in eq 4 with the aid of Gauss' integration method, the integration was limited to the interval $\pm 4(2\sigma^2)^{1/2}/RT$ symmetrically around the maximum of the integrated function. This limitation results in a negligibly small relative error of 10^{-8}. The mean activation energy $\overline{\Delta\epsilon}$ was obtained from Arrhenius-type plots, ln $\bar\nu$ vs $1/T$.

4. Results

4.1. o-Nitrobenzyl Rearrangement in PMMA, PMA, and PSt Matrices. 4.1.1. Determination of Kinetic Parameters.

Figure 2 shows typical kinetic traces recorded with PMMA and PMA films containing oNBB and αMoNBB, respectively. For the evaluation of kinetic data the traces were treated by the two methods described before (vide ante section 3); i.e., the data were plotted according to eqs 3 and 4. Typical plots of log[ln OD_0/OD_t] vs log t are presented in Figure 3. These plots yielded values of the parameters β and α ($\equiv\gamma^\beta$). On the other hand, curve fitting of the kinetic traces on the basis of eq 4 resulted in values of the parameters σ and $\bar\nu$. For example,

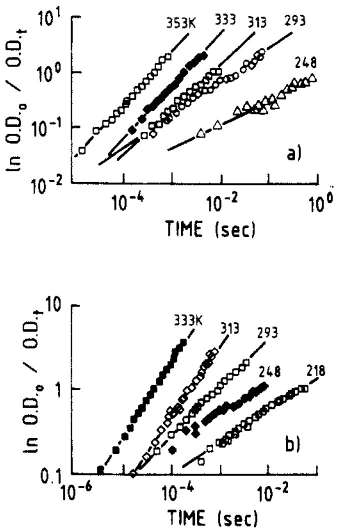


Figure 3. Plots according to eq 3 for oNBB (a) and αPoNBB (b) both in a PMA matrix.

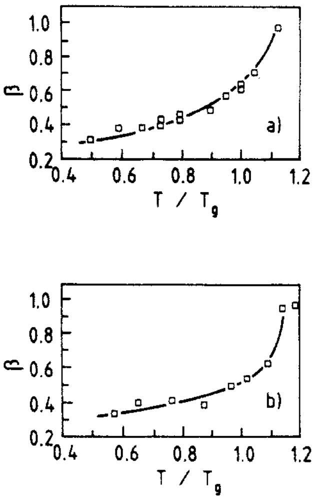


Figure 4. Plot of the dispersion factor β as a function of temperature, obtained with the system oNBB/PMMA.

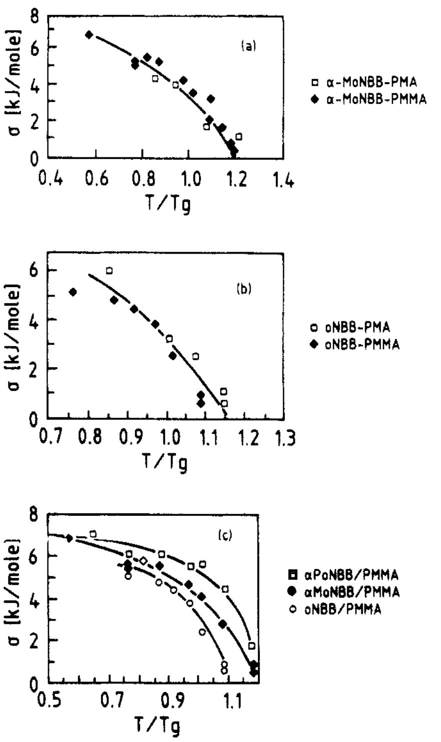


Figure 5. Plots of σ vs the temperature normalized with respect to the glass transition temperature. (a) αMoNBB in PMA and PMMA matrices, (b) oNBB in PMA and PMMA matrices, and (c) oNBB, αMoNBB, and αPoNBB in a PMMA matrix.

the solid lines in Figure 2a,b were obtained by the fitting procedure. Interestingly, in all cases equal numerical values of $\bar{\nu}$ and γ were obtained by both methods, i.e., $\bar{\nu} \equiv \gamma$.

4.1.2. Temperature Dependence of the Dispersion Parameters β and σ. Various results obtained with PMMA and PMA films containing oNBB and αMoNBB, respectively, are shown in Figure 3, where the data are presented in the form of plots according to eq 3. It can be seen that the slope of the straight lines which is proportional to the dispersion factor β increases with increasing temperature. In all cases β approaches unity; i.e., the decay of the nitronic acid follows first-order kinetics at higher temperatures. Notably, these temperatures lie significantly above T_g (about 40 K) which can be seen from Figure 4a,b where typical curves demonstrating the dependence of β on the temperature (here normalized to the glass transition temperature) are depicted. Similar plots of the parameter σ which corresponds inversely to β are shown in Figure 5a–c. It can be seen that σ approaches zero at T/T_g ratios remarkably larger than unity. Moreover, the plots in Figure 5a,b demonstrate that the temperature dependence of the dispersion factor is clearly related to the mobility of the matrix. This is inferred from the fact that the data obtained for the same nitronic acid in a PMA or PMMA matrix, respectively, equally fit the same function $\sigma = f(T/T_g)$, although T_g differs by about 95 K. Despite the relatively large error limit, the influence of the chemical nature of the nitronic acid on the temperature dependence of σ is clearly visible, as can be seen from Figure 5c. All σ values plotted here as a function of temperature were measured in a PMMA matrix. Obviously, at constant temperature the σ values obtained for the substituted nitronic acids are higher than that obtained in the case of the unsubstituted one, and phenyl substitution has a larger effect than methyl substitution. In other words, the transition from dispersive to nondispersive decay kinetics is shifted to higher temperatures in the same order as indicated by the shift of the relevant curves in Figure 5c: The extent to which the curves are shifted is most pronounced in the case of αPoNBB and less pronounced in the case of αMoNBB.

4.1.3. Temperature Dependence of $\bar{\nu}$. The Arrhenius plots shown in Figure 6 concerning the rearrangement of nitronic acids, generated from oNBB, αMoNBB, and αPoNBB, comprise both $\bar{\nu}$ and k_1 values, i.e., $\bar{\nu}$ values obtained at low temperatures where the decay kinetics are dispersive and k_1 values obtained at higher temperatures where the decay kinetics are nondispersive, i.e, following first-order decay laws according to eq 7:

$$c_t/c_0 = \exp(-k_1 t) \tag{7}$$

Notably, both $\bar{\nu}$ and k_1 values fit the same straight lines in all cases. Values of the mean activation energy $\overline{\Delta\epsilon}$ and of the activation entropy ΔS^* were obtained from the slope and the intercept with the ordinate of the straight lines, respectively. It should be pointed out that temperature variations around T_g are not reflected by a change in the slope of the lines. All $\overline{\Delta\epsilon}$ and ΔS^* values are compiled in Tables 3 and 4, respectively. The activation energy of the decay of the nitronic acids in both PMA and PMMA matrices increases in the order αPoNBB < αMoNBB $\ll$ oNBB, indicating that substituted nitronic acids rearrange more easily than the unsubstituted one. Additional

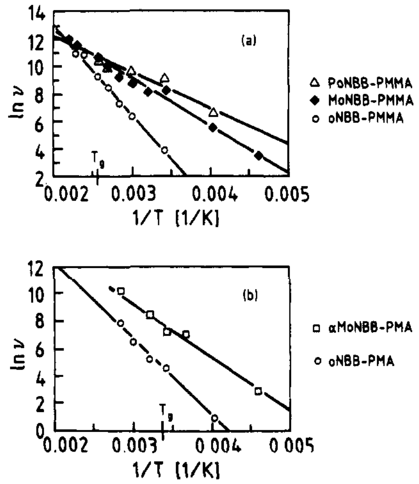


Figure 6. Arrhenius plots (ln ν vs $1/T$) concerning the decay of nitronic acids generated by photolysis of oNBB, αMoNBB, and αPoNBB in a PMMA matrix (a) and in a PMA matrix (b).

Table 3. Activation Energies of $\bar{\nu}$ and k_1 (kJ mol^{-1})

matrix	αPoNB ester	αMoNB ester	oNB ester
PMMA[a]	21 ± 5	28 ± 3	53 ± 5
PMA[a]		32 ± 3	46 ± 2
PSt[a]	16 ± 2		
PDMS[b]	20 ± 3	30 ± 3	53 ± 5

[a] Values obtained with benzoates. [b] Values obtained with isobutyrates at $T > T_g$.

Table 4. Activation Entropies $\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})

matrix	αPoNB ester	αMoNB ester	oNB ester
PMMA[a]	−103 ± 15	−86 ± 10	−33 ± 8
PMA[a]	84 ± 14	−85 ± 10	−49 ± 10
PSt[a]	−109 ± 8		
PDMS[b]	−75 ± 10	−75 ± 10	−30 ± 5

[a] Values obtained with benzoates at $T = T_g$. [b] Values obtained with isobutyrates at $T = 286$ K.

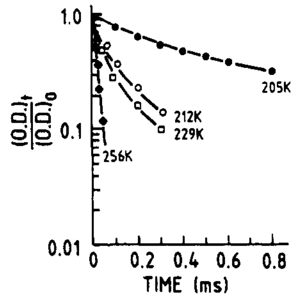


Figure 7. First-order plots of the decay of the OD at $\lambda_{obs} = 440$ nm at various temperatures as indicated in the graph. αPoNBIB (3.41×10^{-4} mol L^{-1}) in PDMS ($M_w = 3.0 \times 10^4$).

experiments were performed with the isobutyrates oNBIB, αMoNBIB, and αPoNBIB in a PMMA matrix. Generally, the results strongly resembled those obtained with the corresponding benzoates and are, therefore, not reported in this paper.

4.2. *o*-Nitrobenzyl Rearrangement in PDMS Matrices. The decay of the nitronic acids follows an exponential (first-order) decay at temperatures above about 230 K. At lower temperatures the decay is nonexponential. Typical results obtained with αPoNBIB in a solution of PDMS ($M_w = 3.0 \times 10^4$) are presented in Figure 7. Figure 8 shows Arrhenius plots of first-order rate constants measured at $T > 230$ K at experiments carried out with oNBIB, αMoNBIB, and αPoNBIB. The activation energies obtained from the slopes of the straight lines are listed in Table 3. They follow the trend also observed at the experiments performed in PMA and PMMA matrices: $\overline{\Delta\epsilon}(\alpha\text{PoNBIB}) < \overline{\Delta\epsilon}(\alpha\text{MoNBIB}) < \overline{\Delta\epsilon}(\text{oNBIB})$. Notably, the activation energies for each nitronic acid determined in the different matrices do not differ very much; i.e., the $\overline{\Delta\epsilon}$ values only slightly depend on the chemical nature of the matrix.

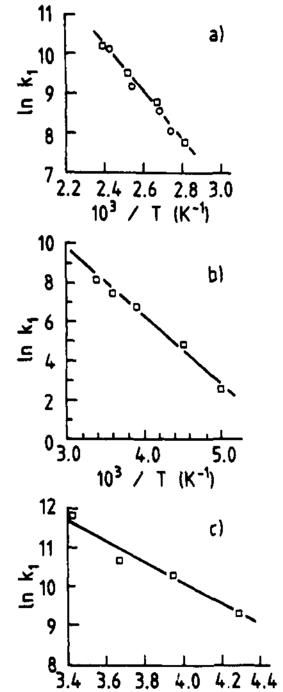


Figure 8. Arrhenius plots (ln k_1 vs $1/T$) concerning the decay of nitronic acids generated by photolysis of oNBIB (a), αMoNBIB (b), and αPoNBIB (c) in a PDMS matrix. [oNBIB] = 4.9×10^{-4} mol L^{-1}, [αMoNBIB] = 5.1×10^{-4} mol L^{-1}, and [αPoNBIB] = 4.4×10^{-4} mol L^{-1}.

When a PDMS sample of higher average molar mass ($M_w = 8.4 \times 10^4$) was used as the solvent, the results were identical to those obtained in the case of the PDMS sample of lower average molar mass ($M_w = 3.0 \times 10^4$).

5. Discussion

This work demonstrates how data evaluation methods based on *dispersive kinetics* can be applied to characterize the kinetics of unimolecular chemical reactions of low molecular compounds in rigid or highly viscous polymeric matrices. It shows how problems related to nonexponential decay kinetics frequently observed can be overcome conveniently and compound-specific parameters such as $\bar{\nu}$ (average rate constant) and $\overline{\Delta\epsilon}$ (mean activation energy) can be obtained.

The interesting feature regarding the rearrangement of the nitronic acids studied in this work is the fact that $\overline{\Delta\epsilon}$ depends only slightly on the chemical nature of the matrix. The relatively low value observed in the case of PSt (system αPoNBB/PSt) as compared to the values found for PMMA and PMA might reflect the weaker interaction of the unpolar PSt matrix with the nitronic acid. In this connection it is interesting to note that results obtained in the case of the merocyanine–spiropyran isomerization led to the conclusion that $\overline{\Delta\epsilon}$ is composed of two parts according to eq 8:[2,11]

$$\overline{\Delta\epsilon} = \overline{\Delta\epsilon}_{\text{compound}} + \overline{\Delta\epsilon}_{\text{matrix}} \tag{8}$$

where $\overline{\Delta\epsilon}_{\text{compound}}$ and $\overline{\Delta\epsilon}_{\text{matrix}}$ denote contributions being inherently connected to the rearrangement and to the influence of the matrix on the rearrangement, respectively. Notably, $\overline{\Delta\epsilon}$ should be approximately equal to $\overline{\Delta\epsilon}_{\text{compound}}$ if measured under conditions where first-order kinetics prevail. In the present work this applies to most of the data obtained in a poly(dimethylsiloxane) matrix, and as can be seen from Table 3, the $\overline{\Delta\epsilon}$ values found for PDMS systems are of the same order as the corresponding values measured with the rigid matrices. Therefore, it follows that $\overline{\Delta\epsilon}_{\text{matrix}}$ does not contribute to or contributes to a minor extent only to $\overline{\Delta\epsilon}$ in the cases studied in this work.

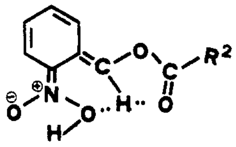
In conclusion, the temperature dependence of the average rate constant of the rearrangement of nitronic acids is essentially determined by $\overline{\Delta\epsilon}_{\text{compound}}$ and not by the mobility of the matrix. This becomes obvious, for instance, by comparing $\bar{\nu}$ values measured in PMA and PMMA matrices at T_g: A difference in T_g of about 90 K corresponds with a difference in $\bar{\nu}$ of about 2 orders of magnitude.

On the other hand, the mobility of the matrix exerts a strong influence on the dispersion factor σ (or β, respectively) as can be seen from the temperature dependence of σ depicted in Figure 5. In this connection it is remarkable that there is no effect of the chemical nature of the matrix on the function $\sigma = f(T/T_g)$, as is demonstrated by Figure 5a,b. On the other hand, this function is significantly influenced by the chemical nature of the α-substituent of the nitronic acid. It can be seen from Figure 5c that the shift of the curves to higher temperatures follows the order oNBB < αMoNBB < αPoNBB which can be related to the increasing bulkiness of the substituent in the α-position.

The Arrhenius treatment of the average rate constants also yields values for $\Delta S^{\ddagger}$, the activation entropy, which are obtained with the aid of eq 9:

$$\nu_0 = \frac{RT}{h} \exp\left[\frac{\Delta S^{\ddagger}}{R}\right] \qquad (9)$$

Here, ν_0 denotes the high-temperature limit of the average rate constant $\bar{\nu}$ according to eq 6. From Table 4 it can be seen that $\Delta S^{\ddagger}$ is negative in all cases. This implies that the activated state is of higher order than the nitronic acid. Actually, this finding supports the existence of a cyclic intermediate which has been suggested earlier[13] (see Scheme 1). Within the rather large error limit an effect of the chemical nature of the matrix on $\Delta S^{\ddagger}$ cannot be detected. However, there is a clearly discernable effect of the chemical nature of the nitronic acid on $\Delta S^{\ddagger}$. Obviously, in the case of the experiments performed with oNBB, $\Delta S^{\ddagger}$ is 2–3 times lower than in the other two cases (αMoNBB and αPoNBB). This might be due to hydrogen bonding which is not possible in the cases of αMoNBB and αPoNBB but is feasible in the case of the unsubstituted compound as can be seen from the following formula:



The hydrogen-bonded structure of the nitronic acid formed from oNBB is of higher order than the non-hydrogen-bonded structures of the substituted nitronic acids which should result in a lower entropy change in the case of the former.

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