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Picosecond and Nanosecond Laser Photolyses of *p*-Nitrophenylacetate in Aqueous Media. A Photoadiabatic Decarboxylation Process?

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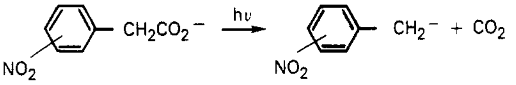
Employing UV picosecond (266 nm, 22 ps, ca. 0.5 mJ) and nanosecond (266 nm, 12 ns, 0.5–5 mJ) excitation, we have investigated the dynamics of the photodecarboxylation of *p*-nitrophenylacetate anions in aqueous solution. In agreement with previous microsecond flash photolysis studies, we believe that the primary decarboxylation products are the *p*-nitrobenzyl anion and carbon dioxide. It is proposed that the anion is produced in its triplet state following photoadiabatic cleavage of the lowest n,π* triplet state of *p*-nitrophenylacetate. The triplet state of the anion is observed as an intermediate (λ_{max} ca. 290 nm) of lifetime 90 ns (pH >5.0). In methanol/water and acetonitrile/water mixtures, its lifetime is found to increase as the aqueous portion of the solvent is decreased. A reaction mechanism is developed.

Margerum et al.[1] first observed the photodecarboxylation of nitrophenylacetic acids in aqueous solutions. Employing steady-state product analysis and microsecond flash photolysis techniques, they concluded that CO_2 elimination occurred from an excited state of the dissociated acid as shown in eq 1. For



(1)

both the *p*- and *m*-nitrophenylacetate anions[2] a quantum yield for decarboxylation of 0.6 was measured; the major final products[1] were *p,p'*-dinitrobibenzyl (with *p*-nitrotoluene as a minor product) and *m*-nitrotoluene, respectively. Under comparable conditions, phenylacetate anions undergo decarboxylation with a quantum yield of only ca. 0.01.[1] Recently, the assignment of the primary products for the *p*-nitrophenylacetate system has been questioned and the *p*-nitrobenzyl radical has been proposed as a primary photodecarboxylation product.[3,4] To clarify this issue and in an attempt to identify the underlying mechanism responsible for the enhanced decarboxylation efficiency, we have investigated the dynamics of the loss of CO_2 from *p*-nitrophenylacetate with improved time resolution (previous studies[1] were limited to the observation of transients present after 20 μs). Our findings suggest that decarboxylation occurs on the triplet energy surface to yield the triplet state of the *p*-nitrobenzyl anion, which is detected as a long-lived (90 ns) intermediate. These studies represent part of a general program in which we seek to characterize, both kinetically and spectrally, transients produced in the excited-state chemistry of various nitro compounds.[5] Our goal is to identify important structure–reactivity trends and to provide an adequate spectral data base for future studies of condensed-phase nitro explosives.

Experimental Section

Materials. *p*-Nitrophenylacetic acid (Aldrich) was recrystallized twice from ethanol/water solutions. Solutions for kinetic study were made by aqueous dilution of freshly prepared 10^{-3} M acid in 1:9 (v/v) methanol:water. The final solutions in stoppered cuvettes generally contained no more than 2% methanol and were adjusted to the appropriate pH with 1 M NaOH or 0.5 M HCl. pH was measured with a Beckman Expandomatic IV pH meter. Solutions were saturated with nitrogen or oxygen by bubbling directly in the photolysis cell.

Apparatus. The nanosecond laser photolysis system has been described previously.[5,6] Excitation was provided by the third (355 nm) or the fourth harmonic (266 nm, 12 ns) of a Nd:YAG laser (Quantel YG 481). Attenuation of the excitation beam was achieved with calibrated metal screen filters. Absorption changes in the first millimeter of photolyzed solution were measured perpendicular to the excitation beam with a pulsed-xenon analyzing lamp. To minimize possible photolysis effects from this beam, two 305-nm cutoff filters were inserted in the analyzing light path in front of the sample cell. Solutions typically were prepared to have an OD_{266} ca. 1.0 for a 1 cm path length.

A more detailed description of the double beam picosecond absorption arrangement is given elsewhere.[7] An active–passive mode-locked Nd:YAG laser system[8] was used to generate ultraviolet pulses (266 nm, 22 ps, ca. 0.5 mJ) which were focused to a 1.5–2 mm diameter spot in a sample cell (MgF_2 windows) of 2 mm path length. The central portion of the photolyzed region was probed with a visible continuum (415–900 nm), generated by focusing the fundamental pulse (1064 nm) into a 15-cm cell of D_2O:D_3PO_4 (1:1). The zero time delay between the photolyzing and the probe pulse was determined by measuring the rise of the peak absorbance of the $S_1 \rightarrow S_n$ absorption spectrum of pyrene in methanol at ca. 470 nm and by measuring the photobleaching of rhodamine 6G. The time at which the signal was half of its maximum value was defined as the origin of the time axis. There was good agreement between the two methods. Aerated solutions were employed with an OD_{266} of between 1.0 and 2.0 for a 2 mm path length. Spectra were obtained by averaging a minimum of 12 laser shots.

The experimental arrangement for pulse radiolysis has also been described previously.[6] Electron pulses of 100-ns duration were delivered to samples contained in a quartz cell of 2.4 cm optical path length. Absorptions of transient species, produced by the pulse, were measured as in the laser system. On-line signal analysis was accomplished with a PDP11/70 minicomputer.

Results and Discussion

Figure 1 shows time-dependent absorption spectra from nanosecond laser photolysis of an N_2-saturated 4×10^{-4} M solution of *p*-nitrophenylacetic acid at pH 11.0. The spectral evolution has an isosbestic point at 315 nm. The experimental points of

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(2) The *o*-nitrophenylacetate anion has a photodecarboxylation yield of 0.04.[1b] We attribute the greatly reduced quantum yield (relative to the para and meta isomers) to competitive intramolecular channels of deactivation associated with the ortho nitro group.

(3) Buncel, E.; Menon, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3499.

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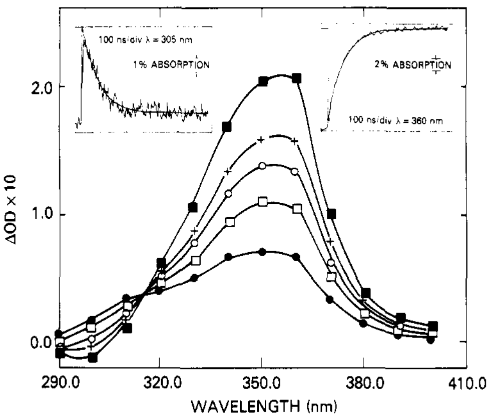

Figure 1. Uncorrected transient absorption spectra recorded after laser photolysis (12 ns, ca. 1 mJ) of an N_2-saturated 4×10^{-4} M aqueous solution of *p*-nitrophenylacetic acid at pH 11.0. (●) 16 ns, (□) 39 ns, (○) 66 ns, (+) 106 ns, (■) 525 ns. The early time spectra have a weak absorption extending throughout the visible. Insets: time-dependent absorption waveforms at 305 nm and 360 nm together with best-fit model exponential curves, $k_F = 1.1 \times 10^7$ s^{-1}.

each spectrum represent the difference between the absorption of the product(s) and that of the parent compound. The insets of Figure 1 display the time dependence of the signal at 305 nm and at 360 nm together with the best-fit exponential curve. The same time constant $k_F = 1.1 \times 10^7$ s^{-1} was determined at each wavelength. Further, similar rate constants were obtained from analysis of waveforms at 340 and at 375 nm. The late term spectrum (λ_{max} ca. 356 nm), which exhibited no decay on our time scales (vide infra) throughout the wavelength range monitored, is essentially identical with that obtained by Margerum et al.[1] in microsecond flash studies. Our data imply that the 356-nm species (N) is formed from a precursor (λ_{max} ca. 290 nm)[9] with a lifetime of 90 ns.

The assignment of the absorption bands of nitrobenzene and some of its derivatives has been the subject of discussion in several publications.[10,11] In the 240–380-nm region, the ground-state absorption spectrum of *p*-nitrotoluene and that of *p*-nitrophenylacetic acid in aqueous solution at pH 11.0 are essentially identical. We infer that 266-nm excitation addresses a charge transfer $\pi \rightarrow \pi^*$ transition localized on the nitrophenyl group. At pH 11.0, ϵ_{355} is ca. 10 times smaller than ϵ_{266}, and excitation at 355 nm may well include a contribution from weak underlying $n \rightarrow \pi^*$ transitions. Nevertheless, for a 10^{-3} M solution of *p*-nitrophenylacetic acid at pH 12.0 containing 10% v/v methanol, excitation at 355 nm produced similar absorption changes at 360 nm ($k_F = 1.1 \times 10^7$ s^{-1}). This suggests that the same reactive state predominates for both the 266- and 355-nm conditions of excitation. Our choice of 266-nm excitation allowed us (i) to observe transient absorption changes without interference from the excitation laser line, (ii) to examine the effect of pH upon the photolysis process,[12] and (iii) to employ low concentrations of *p*-nitrophenylacetate. Over a parent concentration range of 7.2×10^{-6} to 4.0×10^{-4} M, there was no significant change in k_F. We conclude that the essential photodecomposition process is independent of the ground-state concentration of *p*-nitrophenylacetate.

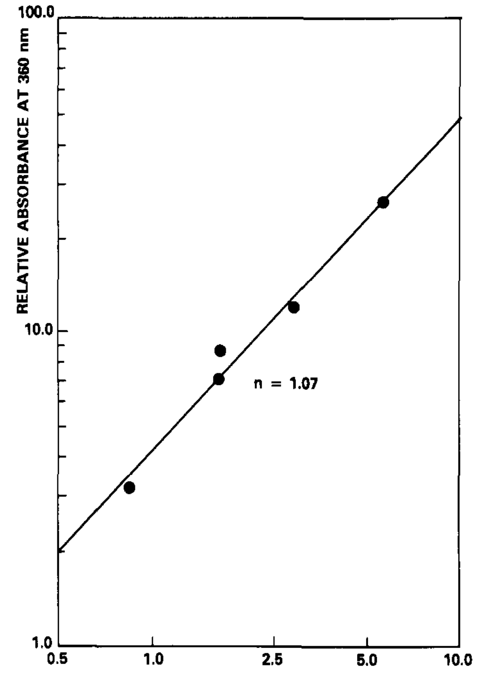

Figure 2. log–log plot of the intensity of absorption at 360 nm vs the laser pulse energy (ca. 0.4–5 mJ). Consistent with a monophotonic process, the slope = 1.07.

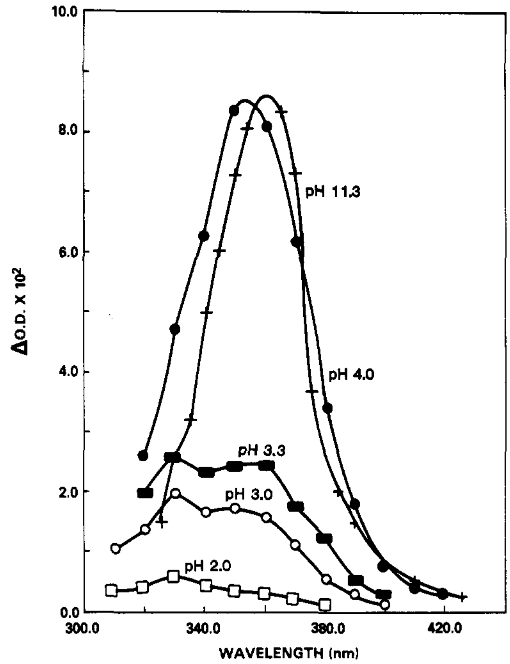

Figure 3. Uncorrected transient absorption spectra recorded 800 ns after laser photolysis of an N_2-saturated 2×10^{-4} M aqueous solution of *p*-nitrophenylacetic acid. (+) pH 11.3, ca. 1 mJ; (●) pH 4.0, 2 mJ; (■) pH 3.3, 3.4 mJ; (○) pH 3.0, 3.4 mJ; (□) pH 2.0, 3.4 mJ.

Figure 2 illustrates that the yield of N at 360 nm has a linear dependence upon the excitation pulse energy (0.4–5 mJ). Lachish et al.[13] have shown that a linear log–log plot (slope = 1) can also be obtained for biphotonic processes within a limited range of light intensities. Such processes may also exhibit a linear plot of yield versus excitation energy but the line will not pass through the origin.[13] In our experiments, a plot of this kind passes through the origin. We conclude, then, that N is generated in this work via a monophotonic process. Furthermore, analyses of waveforms obtained at 360 nm confirm that over our energy range k_F is independent of pulse energy.

Effect of pH. Figure 3 shows uncorrected transient spectra of the late term product(s) at various pH's. The yield decreases with pH; the spectra at pH < 4.0 were obtained with a higher

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(9) This was obtained through extrapolation of spectra to $t = 0$ with correction for ground-state depletion. We assumed a decarboxylation yield of 0.6[1] and that the remaining 40% of the initially produced S_1 states undergo prompt internal conversion to S_0.

(10) Nagakura, S.; Kojima, M.; Maruyama, Y. *J. Mol. Spectrosc.* **1964**, *13*, 174.

(11) Varma, C. A. G. O.; Plantenga, F. L.; Huizer, A. H.; Zwart, J. P.; Bergwerf, Ph.; Van der Ploeg, J. P. M. *J. Photochem.* **1984**, *24*, 133 and references therein.

(12) The absorption spectrum exhibits a blue shift with decreasing pH; this produces an even smaller ϵ_{355}.

(13) Lachish, U.; Shafferman, A.; Stein, G. *J. Chem. Phys.* **1976**, *64*, 4205.

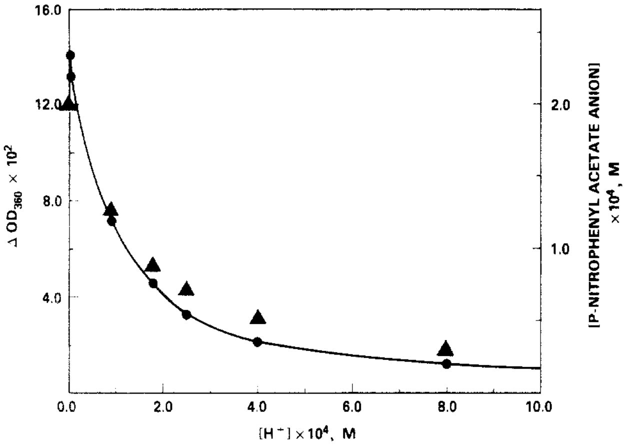

Figure 4. Dependence of the change in absorption at 360 nm (●) upon the H^+ concentration for constant laser energy (12 ns, ca. 2 mJ).[15] The right ordinate gives the corresponding ground-state concentration of *p*-nitrophenylacetate (▲).

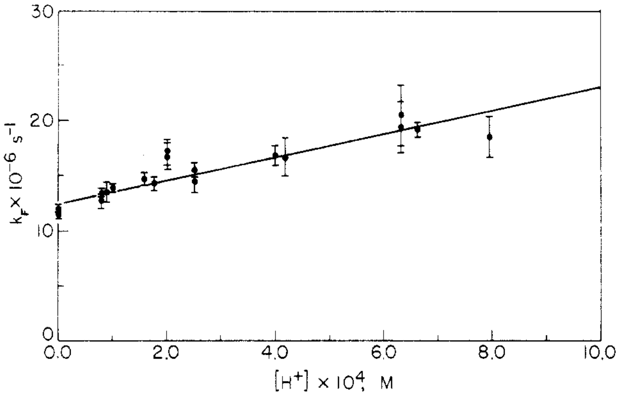

Figure 5. Dependence of the rate constant k_F for formation of the 356-nm absorption upon H^+ concentration. The standard error associated with each determination is indicated. From the slope, a bimolecular rate constant of 1.1×10^{10} M^{-1} s^{-1} is determined.

excitation energy than employed at pH 11.3. The shift of the difference spectrum from pH 11.3 to 4.0, ca. 8 nm, is attributed largely to the influence of the accompanying blue shift of the ground-state parent spectrum. The spectra below pH 3.3 exhibit an additional peak at 330 nm; at pH < 2.0 this is the dominant feature. The signal levels are small at pH ≤3.3; within these limitations we were unable to distinguish between the rate of rise at 330 nm and that at 356 nm. We propose that the 330 nm species is a protonated form of the 356 nm species.

In Figure 4 the yield of N at 360 nm (for constant pulse energy) is plotted against the H^+ concentration. The plot also includes the corresponding concentration of the *p*-nitrophenylacetate anion, based upon a pK_a of 3.85.[14] It is evident that the yield of N is dependent upon the ground-state concentration of the dissociated *p*-nitrophenylacetic acid;[15] an excited state of the parent acetate anion is implicated in the reaction pathway. In support of this, Margerum et al.[1b] observed no photodecarboxylation in various nonaqueous solvents, in acidified ethanol/water solutions, or in acidic aqueous solutions (pH 1.0).

In addition to this static quenching effect, H^+ influences the lifetime of the precursor species below pH 5.0. Figure 5 shows that the rate of formation of the 356-nm transient increases linearly with $[H^+]$; a bimolecular rate constant of 1.1×10^{10} M^{-1} s^{-1} for reaction of the precursor with H^+ can be calculated.

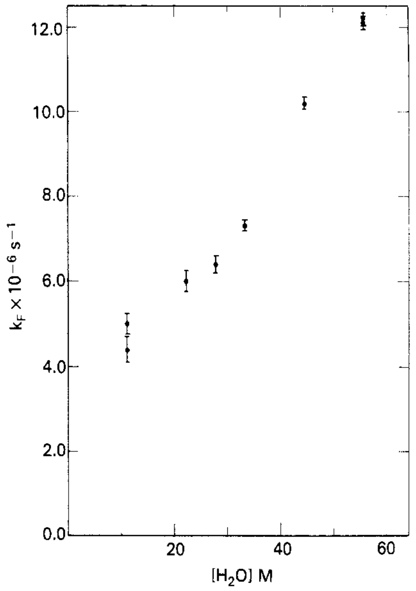

Figure 6. Dependence of k_F upon the concentration of water in methanol/water solutions of *p*-nitrophenylacetic acid (1×10^{-4} M) at pH 11.0. The standard error of each determination is indicated. Note that the points at 55.6 M correspond to the k_F values in aqueous solutions.

Effect of O_2. The rate of production and the yield of the 356-nm species were studied in O_2-saturated solutions. At pH 11.3, k_F (360 nm) = 1.7×10^7 s^{-1} (2×10^{-4} M in the parent) and k_F (305 nm) = 1.5×10^7 s^{-1} (4.1×10^{-4} M). From these measurements, the k_F value in N_2-saturated solution, and that obtained in aerated solution, we determine that the precursor to N is quenched by O_2 with a near-diffusion-controlled rate constant of 4×10^9 M^{-1} s^{-1}. While k_F exhibited a ca. 40% increase in O_2-saturated solutions, the ***yield*** of the 356 nm species was *unchanged*.

Effect of Temperature. Meiggs et al.[16] have demonstrated that the quantum yield of CO_2 from photodecarboxylation of phenylacetate exhibits a strong dependence upon temperature. We have shown that the yield and k_F of the 356-nm absorption do not exhibit a pronounced temperature dependence. From 4 to 55 °C, k_F varies from 1.0×10^7 to 1.7×10^7 s^{-1}; an activation energy of 1.6 kcal mol^{-1} and an A factor of 1.8×10^8 s^{-1} can be calculated.

Effect of Solvent. Varma et al.[11] have observed large variations in the excited-state lifetimes of nitroanisoles in changing from nonpolar to polar solvents: T_1 lifetimes are ca. 1 ns, 35 ns, and 3.5 μs for *m*-nitroanisole in cyclohexane, acetonitrile, and water, respectively. The increase in lifetime in polar solvent was attributed to an increase in π,π^* character of the T_1 state. To examine the possibility of analogous solvent effects upon our long-lived precursor to N, we have studied the photolysis process in various mixed solvent systems.

For N_2-saturated aqueous solutions (ca. 10^{-4} M p-nitrophenylacetic acid, 10^{-3} M NaOH) containing 50% (v/v) methanol, 50% (v/v) acetonitrile, and 80% (v/v) acetonitrile, $k_F = 6.4 \times 10^6$, 5.6×10^6, and 3.0×10^6 s^{-1}, respectively. The solvent dependence is of the opposite sense to that observed by Varma et al.[11] (i.e., the lifetime of the precursor to N *increases* in less polar solvents). Figure 6 indicates that in methanol/water mixtures k_F exhibits a roughly linear dependence upon the concentration of water.[17] The decrease in k_F with increasing mole fraction of methanol is accompanied by a decrease in the yield of the 356-nm absorption. For these solvent mixtures, even in the presence of 10^{-3} M NaOH, the *p*-nitrophenylacetic acid may not be fully dissociated so that the ground-state concentration of *p*-nitrophenylacetate is uncertain. Further, the 356-nm species undergoes a solvent-induced spectral shift (vide infra). Conse-

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[14] *Handbook of Chemistry and Physics*, 64th ed.; Weast, R. C., Ed.; Chemical Rubber Co.: Boca Raton, 1983; p D-168.

[15] The ΔOD_{360} yields in Figure 4 are uncorrected for the effect of pH upon the ground-state absorption spectrum; ϵ_{266} increases with decreasing pH. Further, at low pH no correction has been made for the amount of the 356-nm species which may be present as the 330-nm form. If we assume that each species has a similar ϵ at its wavelength maximum, then the correction is small.

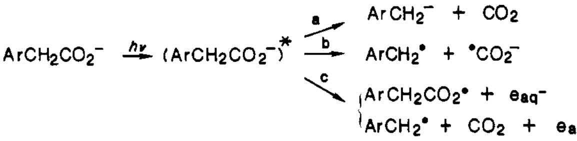
[16] Meiggs, T. O.; Grossweiner, L. I.; Miller, S. I. *J. Am. Chem. Soc.* **1972**, *94*, 7981.

[17] Attempts were made to relate the changes in k_F to the solvent polarity: Plots such as k_F vs dielectric constant (ϵ) and k_F vs the solvent function ($\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$) were superlinear.

quently, it is difficult to relate quantitatively the change in k_F with the change in the yield.

Nature of the 356-nm Species. Assignment of the 356-nm species to the *p*-nitrobenzyl anion by Margerum et al.[1] was based upon an observation by Miller and Pobiner.[18] Following addition of potassium *tert*-butoxide to *p*-nitrotoluene in *tert*-butyl alcohol, the latter workers attributed rapid (3 min) initial formation of absorption at 362 nm to the *p*-nitrobenzyl anion. Chatrousse et al.[19] examined the deprotonation of *p*-nitrotoluene in dimethyl sulfoxide/methanol mixtures, while Buncel et al.[3] studied the process in various aprotic solvents. Both groups concluded that in these solvent systems the absorption maximum of the *p*-nitrobenzyl anion was in the 430–450-nm region. Furthermore, Buncel et al.[4] obtained a very similar spectrum, which was again assigned to the *p*-nitrobenzyl anion, from the thermal decarboxylation of *p*-nitrophenylacetate in dimethyl sulfoxide. This led to speculation that the *p*-nitrobenzyl radical may actually be the primary product of the photodecarboxylation process. Clearly, assignment of the 356-nm species to the *p*-nitrobenzyl anion is based upon data which are, at best, inconclusive and other potential decarboxylation fragments should be considered.

Meiggs and Miller[20] have listed some 25 distinct primary photocleavage modes which are available to a carboxylic acid derivative.[21] Only a few of these pathways, eq 2, have been observed for arylacetates.[16,22] Employing flash photolysis techniques and analysis of final products, Meiggs et al.[16] concluded that process 2a dominates for phenylacetate in methanol, with a minor contribution from (2b). In water it was suggested that (2a) and (2c) are operative. They stressed the potential importance of steps 2b and 2c as realistic photodecarboxylation channels. In an isotopic study of phenylacetate in water, Epling and Lopes[22] concluded that decarboxylation occurs through an ionic mechanism and that the benzyl anion is an essential intermediary. However, they were unable to discount unequivocally process 2c.


(2)

For *p*-nitrophenylacetate, process 2b would yield the *p*-nitrobenzyl radical and the carboxyl radical anion. The *p*-nitrobenzyl radical has been shown to be a product of the unimolecular decomposition of *p*-nitrobenzyl halide radical anions in several chemical,[23] photochemical,[24] and electrochemical[25] studies. Employing the pulse radiolysis technique, Neta et al.[26] have demonstrated that *p*-nitrobenzyl halides efficiently scavenged hydrated electrons to produce initially the parent anion radical which subsequently dehalogenates according to eq 3. The late term

$$XCH_2C_6H_4NO_2 + e_{aq}^- \rightarrow XCH_2C_6H_4NO_2^{\bullet -} \rightarrow X^- + {}^{\bullet}CH_2C_6H_4NO_2 \quad (3)$$

spectrum (λ_{max} = 350 nm), which was also obtained from the reaction of atomic oxygen anions with *p*-nitrotoluene at high pH,[27] was attributed to the *p*-nitrobenzyl radical. The spectrum is very similar to that obtained from pulsed laser excitation of *p*-nitrophenylacetate.

In pulse radiolysis experiments using the same solute concentration and identical solvent conditions to the laser experiments, we have also generated the *p*-nitrobenzyl radical through dissociative electron capture of *p*-nitrobenzyl bromide. The decay kinetics of the radical were second order ($k = 9.6 \times 10^9$ M^{-1} s^{-1}, using $\epsilon_{350} = 1.0 \times 10^4$ M^{-1} cm^{-1} from ref 26a) and were extremely sensitive to oxygen. In contrast, we have witnessed no decay of N (in either O_2- or N_2-saturated 2×10^{-4} M solutions of *p*-nitrophenylacetic acid at pH 11.0) over 400 ms, the instrumental limit of our detection system. Following millisecond flash excitation, we have followed the decay of N in a Cary 219 UV/visible spectrophotometer: a lifetime of ca. 60 s was estimated for N produced from an aerated 3×10^{-5} M solution of *p*-nitrophenylacetic acid at pH 11.0. This value is in good agreement with the previously determined lifetime (53 s)[1] for N following flash photolysis of an aerated $<4 \times 10^{-5}$ M *p*-nitrophenylacetic acid solution at pH 13. Clearly, N cannot be assigned to the *p*-nitrobenzyl radical. Furthermore, we have conducted laser photolysis of *p*-nitrophenylacetate in the presence of the dimer of 2-methyl-2-nitrosopropane, an efficient radical scavenger, and observed no evident decay of N. It appears unlikely that N is a radical species. Our data indicate, then, that process 2b is not a major photodecarboxylation pathway for *p*-nitrophenylacetate in aqueous media.

If channel 2c were the dominant pathway, it could be characterized by the presence of the well-known hydrated electron absorption (λ_{max} = 720 nm).[28] Our essential kinetic information at pH 11.0 has been obtained for pulse energies of ca. 0.5–1.0 mJ; under these conditions no red absorption was recorded. At higher pulse energies (4–8 mJ) a weak red absorption, characteristic of e_{aq}^-, was detected. The intensity of the transient signal exhibited a roughly quadratic dependence upon laser pulse energy. We infer that electron ejection is a biphotonic process and is unimportant for low pulse energies. Process 2c is not a major contributor to the dissociation process under our conditions of excitation.

Alternatively, N may be an intermediate in a photoinitiated chain reaction, and a "steady-state" concentration could provide an account of its apparent long lifetime. Aromatic nitro compounds are known to undergo a series of complex electron-transfer reactions with their one-electron reduction products.[29] In such a picture, the rise time of N should exhibit a dependence upon the parent concentration. Such an effect has been reported for triplet phenylnitrene, which is believed to be a chain propagator in the photoinitiated chain decomposition reaction of phenyl azide.[30] Our kinetic data, which exhibit no dependence upon the *p*-nitrophenylacetate concentration (7.2×10^{-6}–10^{-3} M), obviate the possibility that N can play such a role in the current work. Thus, the abnormally long lifetime of N may well be characteristic of an ion.

In assigning the 356-nm species to the *p*-nitrobenzyl anion, we must account for the apparent large spectral shift observed in aprotic solvents. In fact, anomalously large spectral shifts have been reported for the cyano(*p*-nitrophenyl)methyl anion, produced from deprotonation of *p*-nitrophenylacetonitrile in dimethyl sulfoxide/water mixtures.[31,32] At 0.9 mole fraction of water, an

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absorption maximum was observed at 490 nm; at 0.1 mole fraction it occurred at 535 nm (with a shoulder at 570 nm). It was suggested that there are two forms of the anion: one in which a water molecule is strongly hydrogen bonded to one of the oxygens of the nitro group and the other unspecifically solvated. Further, a large solvent effect upon the absorption spectrum of the photochemically produced 2,4-dinitrobenzyl anion has been observed.[5a,33]

In order to resolve the issue in the current work, we have undertaken laser studies in dimethyl sulfoxide/water and acetonitrile/water mixtures. In these mixed solvent systems, it is evident that the spectrum of N exhibits a large solvent effect: at 0.58 mole fraction of acetonitrile the 356-nm spectrum has a pronounced shoulder at 410 nm, while at 0.86 mole fraction of dimethyl sulfoxide the spectrum shifts to a $\lambda_{\max} = 430$ nm, which is close to the absorption maximum reported for the *p*-nitrobenzyl anion in dimethyl sulfoxide alone.[3,4]

The most reasonable assignment of the 356-nm absorption, then, is to the *p-nitrobenzyl anion*, which like other nitrobenzyl anions in water appears to exist as a "specifically" hydrated form. From studies at pH 4–5, we estimate that the anion reacts with H^+ with a rate constant of ca. 2×10^3 M^{-1} s^{-1}. The 330-nm species, observed at pH < 3.3, is assigned reasonably to the aciquinoid form of *p*-nitrotoluene (in the protonation of the *p*-nitrobenzyl anion, this represents the kinetically favored product). The observations are consistent with a pK_a value of 2–3 for the aci species, which is in good agreement with the value determined for the aci form of *o*-nitrotoluene.[34] As proposed by Margerum et al.,[1] then, we believe that process 2a is the predominant channel of decarboxylation.[35]

Nature of the Precursor. The rise time of the 356-nm absorption represents the decay time (90 ns) of the dissociative excited-state precursor or, if process 2a were an adiabatic photoreaction, the decay time of an excited state of the *p*-nitrobenzyl anion. Such a lifetime is inconsistent with that of a nitroaromatic singlet state.[36] In general, aromatic nitro compounds do not fluoresce (we have observed no emission from *p*-nitrophenylacetate); intersystem crossing is known to proceed rapidly and efficiently (e.g., $\phi_T > 0.6$ for nitrobenzene[36]). The oxygen quenching effect (vide supra) is consistent with a triplet-state precursor but does not rule out a singlet. In principle, triplet–triplet energy-transfer experiments should allow us to determine the multiplicity of the reactive state. Unfortunately, quenching experiments have not been possible; in order to compete effectively with the precursor state decay a high concentration of quencher is required (i.e., a potential quencher must have a relatively small ϵ_{266} and be readily soluble in water). We have been unable to find a molecule which meets both of these criteria. Sensitization experiments have also proved inconclusive: most water-soluble triplet energy sensitizers ($E_T > 60$ kcal mol^{-1}; e.g., 3-benzoylpropionic acid) have substantial $T_1 \rightarrow T_n$ absorption in the region of the *p*-nitrobenzyl anion absorption. In addition, for nitroaromatics intermolecular electron transfer may efficiently compete with triplet–triplet energy transfer.

a. Picosecond Studies. The lowest triplet (T_1) states of nitrobenzene and its derivatives are usually of n,π* character. A lifetime of 90 ns is abnormally long for such a state. The T_1 lifetime of *p*-nitrotoluene, by comparison with nitrobenzene, can be estimated to be no more than ca. 1 ns in isopropyl alcohol.[37] Recently, the lowest triplet state of nitrobenzene and of alkylnitrobenzenes have been identified through picosecond absorption spectroscopy.[38] With excitation at 355 nm, the lowest triplet state of *p*-nitrotoluene in acetonitrile/water (2:5, v/v) mixtures is formed within the laser pulse (rise time of ≤ ca. 5 ps) and decays with a lifetime of ca. 850 ps.[39] The $T_1 \rightarrow T_n$ absorption spectra are characterized by two weak absorption bands at ca. 440 and 625–650 nm.[38]

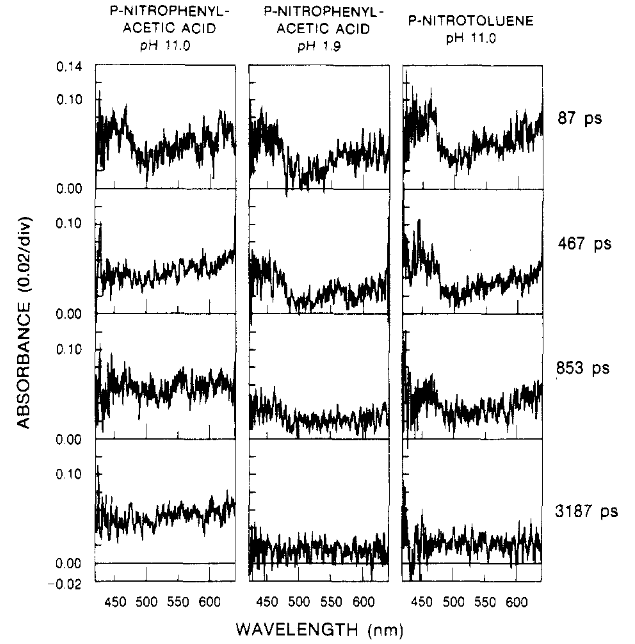

Figure 7. Normalized transient absorption spectra recorded after laser photolysis (22 ps, ca. 0.5 mJ) of aerated 2×10^{-3} M aqueous solutions of *p*-nitrophenylacetic acid and of *p*-nitrotoluene. Average of 12–24 laser shots. Note the characteristic $T_1 \rightarrow T_n$ nitrobenzyl absorption (ca. 450 nm and 625–650 nm),[38] which is observed for all solutions at $t = 87$ ps. At pH 11.0 (column 1), for *p*-nitrophenylacetic acid, the initial spectrum evolves to yield a broad featureless absorption, whereas at pH 1.9 (column 2) it simply decays with a lifetime characteristic of the lowest triplet state of *p*-nitrotoluene (column 3).

Figure 7 (third column) displays our transient absorption spectra at various delay times following picosecond excitation (22 ps, 266 nm) of a 2×10^{-3} M aqueous solution of *p*-nitrotoluene. The spectra exhibit the features characteristic of the weak nitrobenzyl $T_1 \rightarrow T_n$ absorption[38] and they decay with a lifetime consistent with the value measured by Yip.[39] Under the same conditions, the spectra obtained from *p*-nitrophenylacetic acid at pH 1.9 are remarkably similar (see Figure 7, column 2). At this pH there is no decarboxylation. We attribute the spectra to the lowest triplet state of *p*-nitrophenylacetic acid, which appears to have a lifetime similar to that of *p*-nitrotoluene. However, at pH 11.0 (Figure 7, column 1), while the initial spectrum exhibits the characteristic $T_1 \rightarrow T_n$ features, it evolves to yield a broad featureless absorption which shows no decay out to 15 ns (the maximum delay of the picosecond system). We assign this latter absorption to the long-lived (90 ns) precursor identified in the nanosecond experiments, which has weak absorption extending throughout the visible.

The signal levels of the $t = 87$ ps spectra are essentially the same for each system (Figure 7). Assuming that the $T_1 \rightarrow T_n$ extinction coefficients for *p*-nitrotoluene, *p*-nitrophenylacetic acid, and *p*-nitrophenylacetate are similar, we infer that each molecule has a similar triplet yield (i.e., for *p*-nitrophenylacetate there are no additional deactivation channels which can compete effectively with singlet–triplet intersystem crossing). The major difference

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[35] Knowing the laser pulse energy, the interrogated volume, and assuming a quantum yield of 0.6,[1] we can estimate an extinction coefficient at 356 nm for the *p*-nitrobenzyl anion of $\geq 2.0 \times 10^4$ M^{-1} cm^{-1}. The *p*-nitrobenzyl radical (produced according to process 2b) and the solvated electron (2c) have similarly large extinction coefficients at their respective absorption maxima. If these species were present at a level of ca. 5% of the *p*-nitrobenzyl anion, they would have been detectable. We may conclude that, under our conditions, ≥90% of the decarboxylation process occurs through channel 2a.

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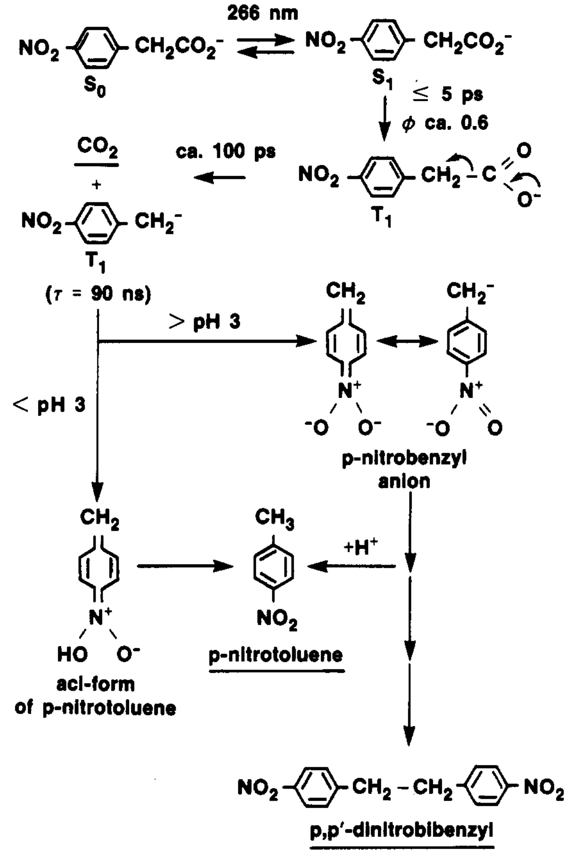
between the *p*-nitrophenylacetate spectra at longer delays and the initial spectrum amounts to a small net increase of signal at around 500 nm. The poor signal-to-noise precludes a meaningful kinetic study. However, we suggest that the spectral evolution is essentially complete by the 467-ps frame. At this delay the characteristic $T_1 \rightarrow T_n$ features have disappeared to yield the broad featureless absorption. This is evidence against a singlet-state mechanism, since the *p*-nitrophenylacetate S_1 lifetime is ≤ 5 ps (from the $T_1 \rightarrow T_n$ rise time). It is proposed then that the lowest triplet state of *p*-nitrophenylacetate is the progenitor of the long-lived precursor to N.

Two alternative pictures may then be offered for the long-lived precursor: (i) a triplet state of the *p*-nitrobenzyl anion, or (ii) a charge-transfer species in which there is electron transfer from the carboxylate group to the nitrophenyl group.[40] Rapid intramolecular charge transfer has been proposed as the primary step in the photo-Smiles rearrangement of *N*-[ω-(*p*-nitrophenoxy)alkyl]anilines.[42] More recently, intramolecular electron transfer has been postulated to account for a long-lived intermediate observed in the photodephosphorylation of *p*-nitrobenzylphosphonate.[43] In our work, for a charge-transfer intermediate, its decay rate k_F would reflect fragmentation to the *p*-nitrobenzyl anion and carbon dioxide. In this picture, there is no reasonable account of the observed O_2 and solvent effects. A more immediate explanation of these effects arises through assignment of the precursor to the triplet state of the *p*-nitrobenzyl anion.[44] Oxygen quenching of the triplet state amounts to an additional deactivation mode leading to the ground-state anion. Thus, an enhanced decay rate is observed in O_2-saturated solution while the yield of the ground-state *p*-nitrobenzyl anion is unchanged. Also, this is consistent with the work of Margerum et al.,[1] who observed essentially no change in the quantum yield of decarboxylation in going from N_2-saturated to O_2-saturated solutions. Efficient $T_1 \rightarrow S_0$ intersystem crossing in aqueous media is proposed to account for the solvent effects upon the decay rate of the triplet state of the *p*-nitrobenzyl anion. The low activation energy and low *A* factor, determined from the temperature studies, are consistent with a triplet–singlet intersystem crossing process.[45] While our data indicate that the ground-state anion exists as a "specifically" hydrated form, the nature of the solvent interaction in the triplet state is unclear. Based on the normally short triplet lifetimes of nitrobenzyl derivatives, we suggest that the triplet state of the *p*-nitrobenzyl anion has substantial π,π^* or charge-transfer character.[11] The proposed reaction mechanism is outlined in Scheme I,[46] where the *p*-nitrobenzyl anion can be viewed as a photoactivated leaving group. This mechanism is consistent with the observation that the undissociated acid does not undergo decarboxylation.

SCHEME I: Proposed Reaction Mechanism following 266-nm Excitation of *p*-Nitrophenylacetate[a]



[a] The final products[1,46] are underlined.

b. Additional Evidence for a Triplet Adiabatic Photoreaction. Further support for a decarboxylation process proceeding through the triplet state is found in quantum yield measurements. As mentioned above, quantum yields of triplet formation are high, ca. 0.6, for aromatic nitro compounds.[36] A quantum yield of 0.6 has been determined for the photodecarboxylation of *p*-nitrophenylacetate.[1b] This is consistent with a triplet-state mechanism in which nearly all triplets undergo decarboxylation (i.e., radiationless deactivation does not compete with CO_2 loss). Our picosecond spectra corroborate this point.

There is an increasing amount of evidence in the literature to suggest that nitroaromatics exhibit unusual photochemistry in aqueous media.[47,48] Recently, Wan and Muralidharan[49] have observed an interesting class of reactions for 2-(*p*-nitrophenyl)ethanols and related nitrobenzyl derivatives in aqueous acetonitrile. They suggested that the reaction occurred through a triplet-state mechanism to yield initially the *p*-nitrobenzyl anion. The final isolable nitro products of this reaction from N_2-saturated solutions are *p,p'*-dinitrobibenzyl and *p*-nitrotoluene, the same products isolated from the photodecarboxylation of *p*-nitrophenylacetate.[1] Employing short-pulse laser spectroscopy, we have examined the rate of formation of the *p*-nitrobenzyl anion for several of these *p*-nitrobenzyl derivatives in aqueous acetonitrile solutions. In each case, the *p*-nitrobenzyl anion was detected,[50] formed from a

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(40) Both processes are reasonable on energetic grounds. Unfortunately, the heats of formation of *p*-nitrophenylacetate and the *p*-nitrobenzyl anion are not known, but we can estimate that reaction 2a, as a ground-state process, is endoergic by ca. 20 kcal mol^{-1}. Process (i) will be thermoneutral if the triplet state of the *p*-nitrobenzyl anion lies ca. 20 kcal mol^{-1} below that of *p*-nitrophenylacetate. Inspection of the ground-state ($S_0 \rightarrow S_1$) absorption spectra of *p*-nitrophenylacetate and the *p*-nitrobenzyl anion indicates that such a difference in not unreasonable. The ground-state energetics of process (ii) can be crudely estimated as 62 kcal mol^{-1} (2.7 eV), from the half-wave reduction potential of *p*-nitrotoluene and oxidation potential of, e.g., tetrabutylammonium acetate, −1.2 and 1.5 eV vs SCE, respectively.[41] Thus, intramolecular electron transfer from the carboxylate group to the nitrophenyl group in the triplet state (E_T ca. 60 kcal mol^{-1})[36,38] is supportable energetically.

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(44) In principle, a two-pulse laser experiment might confirm the presence of the triplet state of the *p*-nitrobenzyl anion as an intermediate in this system. Following a 266-nm dissociative pulse, 355-nm excitation of the *p*-nitrobenzyl anion would populate the triplet state provided there is a reasonable $S_1 \rightarrow T_1$ intersystem crossing efficiency. Its existence would be confirmed through recovery of the ground-state anion with a rate constant of 1.1×10^7 s^{-1}. In fact, experiments of this kind have been inconclusive. To some extent, this is because the 355-nm pulse also causes decarboxylation of the parent.

(45) Rate constants for intersystem crossing typically exhibit low activation energies and low preexponential factors; see, e.g.: Wilkinson, F. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1975; Vol. 2, Chapter 3.

(46) Work is now in progress to examine the decay kinetics of the *p*-nitrobenzyl anion. Our preliminary indications are that decay of the anion involves competition between protonation (pseudo first order to give *p*-nitrotoluene) and dimerization (second order to yield ultimately the bibenzyl compound). See also, Craig, B. B.; Pace, M. D. *J. Chem. Soc., Chem. Commun.* **1987**, 1144.

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J. Phys. Chem. 1987, 91, 5912–5921

precursor whose spectral and temporal characteristics are essentially the same as those for precursor in the *p*-nitrophenylacetate system: λ_{max} ca. 290 nm and k_F ca. 1.0×10^7 s^{-1}. We suggest that the same precursor is present in these systems, i.e., the triplet state of the *p*-nitrobenzyl anion. Furthermore, in the dephosphorylation of *p*-nitrobenzylphosphonate[43] the *p*-nitrobenzyl anion is also formed with a rate constant of 1.2×10^7 s^{-1}. Although the precursor species was postulated to be a charge-transfer state of *p*-nitrobenzylphosphonate, given the present data, a more compelling assignment might be the triplet state of the *p*-nitrobenzyl anion, formed following photoadiabatic cleavage.

In summary, the same rate of rise for the *p*-nitrobenzyl anion from these diverse *p*-nitrobenzyl derivatives provides strong evidence to support the triplet state of the anion as a common intermediate in these systems and counterindicates a charge-transfer mechanism. Efficient, rapid $S_1 \rightarrow T_1$ intersystem crossing within the nitroaromatic parent followed by spin-controlled dissociation then accounts for photoelimination of the *p*-nitrobenzyl anion on the lowest triplet energy surface.

Conclusion

We have detected a long-lived (90 ns) species in the laser photodecarboxylation of *p*-nitrophenylacetate in aqueous media. In our preferred picture, it is attributed to the triplet state of the *p*-nitrobenzyl anion which is formed following loss of CO_2 from the triplet state of the parent *p*-nitrophenylacetate. The decay kinetics of the *p*-nitrobenzyl anion triplet state exhibit a strong dependence upon solvent. In agreement with the work of Margerum et al.,[1] the major primary decarboxylation products are then the *p*-nitrobenzyl anion and CO_2. To account for the blue-shifted absorption band of this anion, we suggest that, like other nitrobenzyl anions[5a,31–33] in aqueous media, the nitro group is specifically hydrated. There is evidence to suggest that the photoelimination of the *p*-nitrobenzyl anion from other *p*-nitrobenzyl derivatives may occur via adiabatic pathways.

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Registry No. CO_2, 124-38-9; *p*-nitrophenylacetate anion, 3545-74-2; *p*-nitrobenzyl anion, 72409-67-7.

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Preparation of Mono- or Zerovalent Nickel by Single or Successive One-Electron-Transfer Steps in the Photoreduction of Silica-Supported Nickel Catalysts

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Ni/SiO_2 supported catalysts prepared by competitive cation exchange can be reduced by UV irradiation in hydrogen at 77 K to lead by a one-electron process to Ni^+ species. These Ni^+ ions which exhibit an EPR signal at $g_1 = 2.68$, $g_2 = 2.32$, and $g_3 = 2.007$ and a band at 838 nm in the UV–vis and near-IR reflectance spectra bind molecular hydrogen to form $[\equiv Ni(H_2)]^+$ pseudotetrahedral surface complexes. The photoreduction process in carbon monoxide occurs appreciably only at 25 °C and depends on the CO pressure. It is a one-electron-reduction process, and $[Ni(CO)_n]^+$ species ($n = 2$–4) are observed by EPR and IR for pressures above 10 Torr. For lower pressures, the formation of metal is observed by IR and ferromagnetic resonance via the reduction by two consecutive one-electron-transfer steps. The first step proceeds from the photoproduction of $(Ni^+–O^-)^*$ excited states. The second step is due to the release of electrons from a reservoir which has been tentatively identified to pseudo-carbonates characterized by IR bands at 1750–1850 cm^{-1} and by TPD peaks of CO at 803 K and of CO_2 at 513 and 803 K. The formation of the latter species is the result of the quenching of the excited state by CO molecules which react with the O^- activated surface oxygens to lead to CO_2^- which with O^{2-} ions generates CO_3^{3-} radical ions. The very weak EPR signal for those radicals suggests their recombination to form diamagnetic dimers. Although the thermodynamics is highly favorable in both cases, the photoreduction is more efficient in H_2 than in CO where kinetics limitations could occur either from the migration process of the CO_3^{3-} radicals or from the sterically demanding site of the pseudo-carbonates.

Introduction

Earlier work of this laboratory has shown that Ni^+ ions produced by mild reduction of Ni^{2+} ions deposited in zeolites or on silica by a competitive cation-exchange method[1–5] were the active sites in the reaction of oligomerization of olefins,[6,7] and this has been recently confirmed.[8,9] Unfortunately, the content of Ni^+ ions in the various systems investigated amounts only to a few percent of the total nickel deposited so that the improvement of

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