

$10^{10} \text{ M}^{-1} \text{ s}^{-1})^{13}$ is at the upper end of the diffusion-controlled limit.

References and Notes

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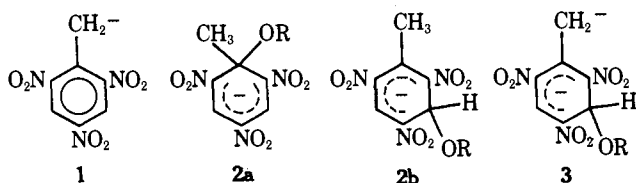
Proton-Transfer and Electron-Transfer Processes in Reaction of *p*-Nitrotoluene with Bases. A Spectrophotometric Study¹

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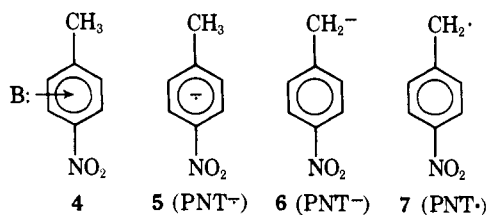
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Abstract: The interaction of *p*-nitrotoluene (PNT) with a variety of basic systems has been studied spectrophotometrically. The bases employed, in decreasing order of base strength, were potassium hydride, dimethyl potassium, triphenylmethylpotassium, fluorenylpotassium, and potassium *p*-nitroanilide, while the solvents used were dimethyl sulfoxide, tetrahydrofuran, and dimethoxyethane, with 18-crown-6 ether present in the latter two cases. The major species produced in the reactions were *p*-nitrobenzyl anion (PNT⁻), *p*-nitrotoluene radical anion (PNT^{•-}), and *p,p'*-dinitrostilbene radical anion (DNS^{•-}). The principal processes in the PNT-base systems are believed to be (i) PNT + B⁻ ⇌ PNT⁻ + BH; (ii) PNT + B⁻ ⇌ PNT^{•-} + B•; (iii) PNT⁻ + PNT ⇌ PNT• + PNT^{•-}. DNS^{•-} is formed through secondary processes via *p,p'*-dinitrobenzyl. Discussion of process (i) is given in terms of the relative pK_as of PNT and the respective BH species, while (ii) is analyzed on the basis of the reduction potential of PNT and the oxidation potential of B⁻. For the case of the PNT/Ph₃C⁻ system, the electron-transfer process (ii) is kinetically preferred but this equilibrium is rapidly established. On the other hand the proton-transfer process (i) is greatly favored thermodynamically and is effectively irreversible; as a result the proton transfer predominates. This is in accord with observation of PNT⁻ as the initially formed species in this system. The processes occurring in the other base systems are similarly analyzed. The assignment of the absorption due to the *p*-nitrobenzyl anion is at variance with an earlier literature report deduced from examination of the PNT/*t*-BuOK/*t*-BuOH system. Electron-transfer and proton-transfer processes in the PNT/*t*-BuO⁻ system are also discussed.

The interaction of aromatic nitro compounds with bases can give rise to processes involving charge transfer, electron transfer, proton transfer and σ -complex formation, as well as to nucleophilic substitution when a displaceable group is present.²⁻⁹ In the case of 2,4,6-trinitrotoluene interacting with alkoxide bases, we have identified and studied in detail the processes involving proton transfer yielding the 2,4,6-trinitrobenzyl anion (1) and σ -complex formation resulting in adducts 2a or 2b.¹⁰⁻¹² Under other conditions, the dianion 3 has also been identified.¹³



The *p*-nitrotoluene (PNT)-base system has been especially challenging in that, whereas stable σ complexes have apparently not been observed, the processes involving charge transfer (4), electron transfer (5), and proton transfer (6), as well as free-radical species (7), have all been reported.¹⁴⁻¹⁶ However,



the system is complicated by the instability of these species as generated under typical reaction conditions; the product which is isolated in the reaction of PNT with alkoxide ion is actually *p,p'*-dinitrobenzyl (DNBB, 8) or *p,p'*-dinitrostilbene (DNS,

Table I. Spectral Species Formed in Reaction between *p*-Nitrotoluene (PNT) and Bases (R⁻K⁺) in Various Solvents

expt	R ⁻ K ⁺	solvent	[R ⁻ K ⁺] × 10 ³ , [PNT] × 10 ³ , [18-crown-6],			λ _{max} (Å)		
			M	M	M	1st species ^b	2nd species ^c	3rd species ^d
1	H ⁻ K ⁺ ^a	DME	77.5	1.262		580 (0.1), 550 (0.04)		
2	H ⁻ K ⁺ ^a	THF	34.1	0.985		580 (0.1), 550 (0.05)		
3	H ⁻ K ⁺ ^a	DME	27.3	0.967	0.0318	428 (1.84)	328 (1.18)	582 (0.46), 626 (1.22)
4	H ⁻ K ⁺ ^a	THF	70.7	0.752	0.0470	430 (1.80)	330 (1.23)	475-575 (0.32)
5	Ph ₃ C ⁻ K ⁺	DME	0.516	1.170	0.0321	428 (2.0)	327 (1.74)	580 (0.46), 624 (0.97)
6	Ph ₃ C ⁻ K ⁺	Me ₂ SO	0.350	0.673		450 (1.43)	328 (1.16)	615 (0.21), 654 (0.26)
7	dimethyl K ⁺	Me ₂ SO	39.9	0.929		450 (0.81)	380 (0.92)	550-700 (0.56)
8	Fl ⁻ K ⁺	Me ₂ SO	0.940	1.670		450 (0.68)	330 (0.90)	615 (0.50), 654 (1.57)
9	PNA ⁻ K ⁺	Me ₂ SO	0.206	0.757				

^a Concentration calculated from total KH added; solution is heterogeneous. ^b Species identified as PNT⁻K⁺, except in experiments 1 and 2; see text. ^c Species identified as PNT⁻·K⁺, except in experiment 7; see text. ^d Species identified as DNS⁻·K⁺, except in experiments 4 and 7, where the spectral changes were more complex; see text.

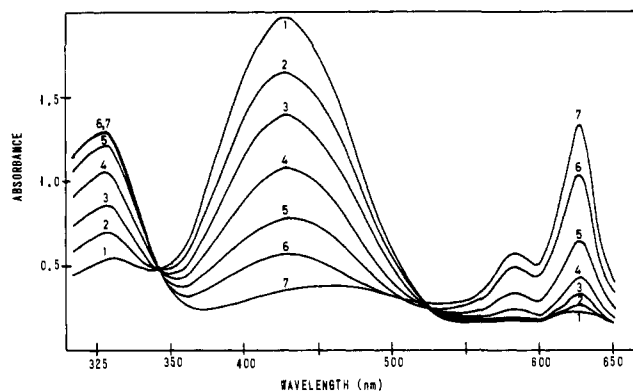


Figure 1. Variation of absorption spectra of a reaction solution consisting of PNT/KH/18-crown-6 in DME, as a function of time: spectrum 1, 3 min; 2, 7 min; 3, 11 min; 4, 17 min; 5, 27 min; 6, 45 min; 7, 89 min.

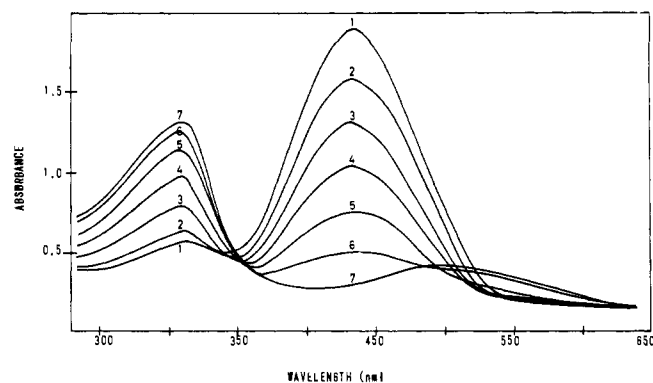
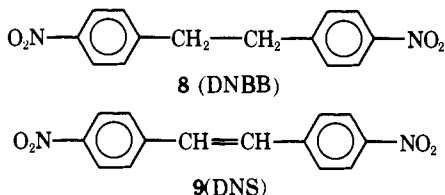


Figure 2. Variation of absorption spectra of PNT/KH/18-crown-6 in THF as a function of time: spectrum 1, 3 min; 2, 11 min; 3, 19 min; 4, 29 min; 5, 45 min; 6, 134 min; 7, 180 min.



9). Since **8** and **9** can give rise to proton-transfer and electron-transfer processes, respectively, while **4**–**7** can further interact with each other in various combinations to give yet other metastable species, the assignment of the transient spectra in the PNT–base system can be exceedingly complicated as well as risky.

As part of our work on the spectroscopic study of arylmethyl carbanions,^{17–21} and the nitrobenzyl carbanions in particular,^{1,9–11} we have extended our studies to include the PNT–base system. We report now the results of the study for a variety of base and solvent systems, using mainly UV–visible absorption spectroscopy, though some supporting ESR experiments have also been performed. While an extensive ESR study of PNT–alkoxide systems has previously been reported,^{14–16} only preliminary results of a UV–vis spectral study have been given so far, for the limited case of PNT reacting with *tert*-butoxide ion in *tert*-butyl alcohol.²² It can be stated that our main conclusions are in accord with the study by Russell and Janzen using ESR spectroscopy,^{14–16} but not with the UV–vis spectral study of Miller and Pobiner.²²

Results

We have investigated the interaction of PNT with the following base systems: potassium hydride/dimethoxyethane (DME) or tetrahydrofuran, both in absence and in presence

of 18-crown-6 polyether; triphenylmethylpotassium (TPM⁻K⁺) in DME in presence of 18-crown-6; TPM⁻K⁺ in dimethyl sulfoxide (Me₂SO); dimethyl potassium in Me₂SO; fluorenyl potassium (Fl⁻K⁺) in Me₂SO; potassium *p*-nitroanilide (PNA⁻K⁺) in Me₂SO. In the majority of the experiments UV–visible absorption spectroscopy alone was used to monitor the course of reaction but in selected experiments ESR spectroscopy was used concurrently. The methods and apparatus used for spectral measurement under anaerobic conditions were adapted from our work on the spectroscopic studies of arylmethyl carbanions;^{17–21} details of procedures, etc., are given in the Experimental Section.

The treatment of PNT with KH in DME or THF gave rise to a pale red solution having a small absorption at 580 nm (sh 550) (experiments 1 and 2 in Table I). No further spectral changes were observed over 24 h. Therefore, the following set of experiments were performed in the presence of 18-crown-6 polyether, which was expected to enhance the reactivity of the hydride due to complexation of K⁺.²³ This expectation was borne out, since it was found that under these conditions, in DME solvent, a yellow-colored solution was immediately obtained having a strong absorption at 428 nm (experiment 3). This absorption decreased gradually while simultaneously there evolved one new absorption at 328 nm and another double absorption at 582 and 626 nm with the longer wavelength maximum being the more intense. The 328 and 582/626 nm absorptions evolved at different rates, the former reaching maximum after 45 min and the latter after 2 h, indicating that they correspond to different species. The final green-colored solution also contained a residual broad absorption in the 400–500-nm region and was stable for ~24 h. Selected spectral scans obtained during the experiment are shown in Figure 1.

The PNT/KH/18-crown-6/THF system (experiment 4)

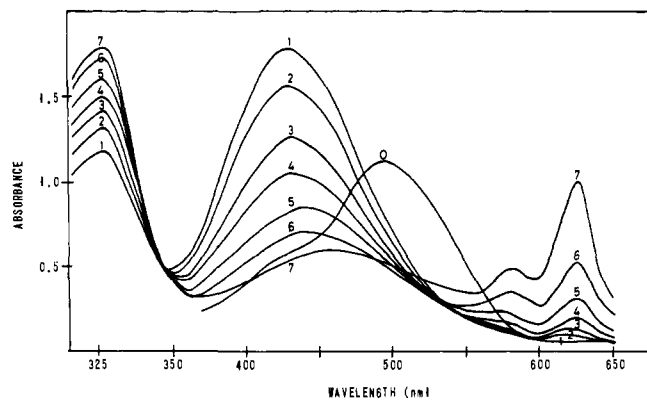


Figure 3. Variation of absorption spectra of PNT/ $\text{Ph}_3\text{C}^-\text{K}^+$ /18-crown-6 in DME as a function of time: spectrum 0, $\text{Ph}_3\text{C}^-\text{K}^+$; 1, 9 min; 2, 11 min; 3, 15 min; 4, 19 min; 5, 27 min; 6, 39 min; 7, 77 min. PNT introduced after spectrum 0 is recorded.

showed similarity as well as differences with respect to the analogous basic system but using DME solvent as discussed above. The common feature was the immediate appearance on mixing of a strong absorption at 430 nm which slowly decreased in intensity while an absorption at 330 nm increased in intensity reaching maximum value after 2 h. However, contrasting with the previous system, in the present case the long-wavelength absorption which appeared simultaneously consisted of a small, broad band covering the 475–575-nm region. The final spectrum was stable for ~ 24 h. Representative spectra for this reaction as a function of time are given in Figure 2.

The reaction of PNT with the triphenylmethyl carbanion was examined next. TPM^-K^+ in DME was conveniently prepared by action of KH on triphenylmethane (TPM) in presence of 18-crown-6 ether²⁰ followed by filtration to remove the excess KH. Addition of PNT to the TPM^-K^+ solution resulted in the immediate discharge of the TPM^- absorption at 492 (sh 432) nm and the formation of a strong absorption at 428 nm (experiment 5). The sequence of events which followed was fully analogous to that observed in the PNT/KH/crown/DME system described above, namely, the decline of the 428-nm absorption and the emergence of the 327- and 624/580-nm peaks, as well as the broad absorption in the 400–500-nm region (see Figure 3).

Use of TPM^-K^+ but changing the solvent to Me_2SO (the TPM^-K^+ being obtained from reaction of TPM with a deficiency of dimsyl potassium) led to qualitatively similar results as in the DME system but there was a significant shift in some of the absorption maxima (experiment 6). The initial absorption, following the disappearance of the TPM^-K^+ spectrum, now occurred at 450 nm and as this peak gradually diminished there was an accompanying bathochromic shift, leaving a residual absorption centered at ~ 480 nm. The low-wavelength peak which emerged simultaneously occurred at 328 nm, closely similar to that in the TPM^-K^+ /DME system, but the double absorption appearing at longer wavelength now occurred at 615/654 nm, being appreciably displaced to longer wavelengths. Selected spectra are shown in Figure 4.

Reaction of dimsyl potassium with PNT (experiment 7) gave rise to an initial absorption at 450 nm which decreased over ~ 20 min while an absorption at 380 nm increased in intensity, Figure 5. Thereafter the 380-nm absorption started diminishing while simultaneously a complex series of changes was observed in the 550–700-nm region. In the course of 2 h an initial broad absorption with a maximum at ~ 640 nm, shoulder 690 nm, was replaced by another absorption with maximum at 585 nm, shoulder 620 nm. It can be noted that the dimsyl anion has a strong absorption in the 325-nm region, thereby effectively blanking out the 300–350-nm region, with

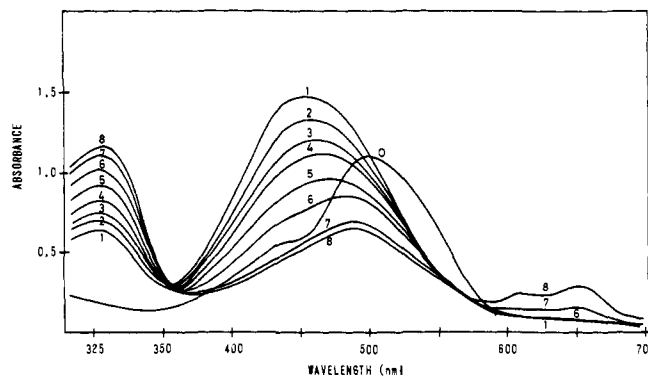


Figure 4. Variation of absorption spectra of PNT/ $\text{Ph}_3\text{C}^-\text{K}^+$ in Me_2SO as a function of time: spectrum 0, $\text{Ph}_3\text{C}^-\text{K}^+$; 1, 3 min; 2, 7 min; 3, 11 min; 4, 17 min; 5, 27 min; 6, 43 min; 7, 59 min; 8, 79 min.

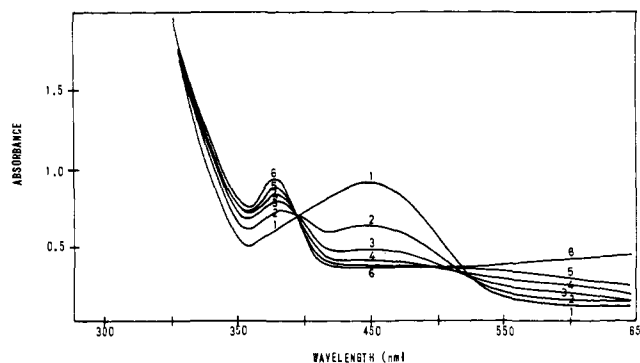


Figure 5. Variation of absorption spectra of PNT/dimsyl potassium in Me_2SO as a function of time: spectrum 1, 5 min; 2, 7 min; 3, 9 min; 4, 11 min; 5, 13 min; 6, 15 min.

the result that the ~ 330 -nm absorption observed in the basic systems discussed earlier would not be visible with dimsyl present. However, the initially observed absorption at 450 nm in this system is significant and will be referred to again later.

The PNT/ Fl^-K^+ / Me_2SO system (experiment 8) exhibited somewhat different and interesting behavior relative to the systems described hitherto. Thus the main peak of Fl^-K^+ in Me_2SO , appearing at 372 nm, started decreasing in intensity on addition of PNT while a new peak at 450 nm increased in intensity. The smaller broad peak of Fl^-K^+ , centered at 480 nm, now appeared as a shoulder on the long-wavelength side of the growing 450-nm absorption and this shoulder absorption also became less pronounced. The 450-nm absorption reached a maximum value 15 min after mixing and then started decreasing. Simultaneously, a shoulder absorption at ~ 330 nm and a double absorption at 615 and 654 nm was increasing in intensity; the long-wavelength absorptions continued to grow after the ~ 330 -nm shoulder absorption had reached constant value. Thus the Fl^-K^+ system is the first one in the series of basic systems examined in which initial development of the 450-nm absorption could be observed. Selected spectra are shown in Figure 6.

In the PNT/*p*-nitroanilide system, the trend which began when Fl^-K^+ was used as base became even more accentuated. Thus addition of PNT to PNA^-K^+ / PNA (1:1) in Me_2SO resulted in an extremely slow reaction, $\sim 8\%$ during 6 h (experiment 9, Figure 7). Owing to the strong absorption of PNA^-K^+ in the 430–500-nm region, there was no apparent emergence of a 450-nm absorption as found with the other bases in Me_2SO medium. However, that some reaction did in fact occur could be seen by an increase of the absorption at 388 nm due to free PNA and a smaller decrease of the absorptions at 467 and 495 nm due to PNA^-K^+ (in accord with the extinction coefficient values of PNA at 390 nm (16 000) and

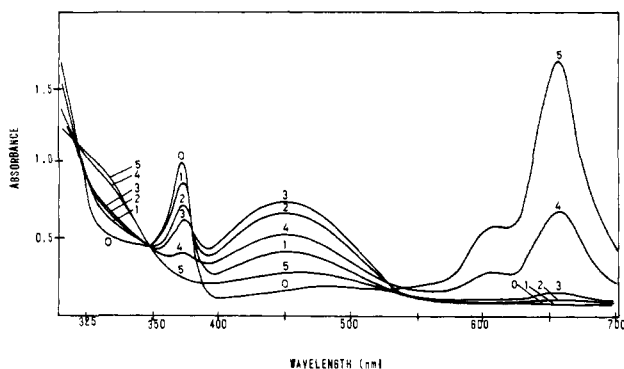


Figure 6. Variation of absorption spectra of PNT/Fl-K⁺ in Me₂SO as a function of time: spectrum 0, Fl-K⁺; 1, 3 min; 2, 7 min; 3, 11 min; 4, 37 min; 5, 200 min.

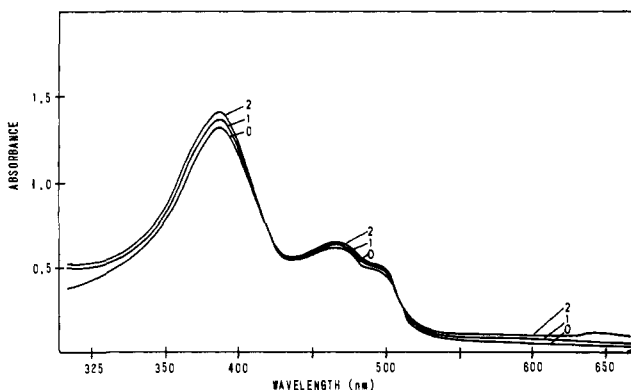


Figure 7. Variation of absorption spectra of PNT/PNA-K⁺ in Me₂SO as a function of time: spectrum 0, PNA-K⁺; 1, 180 min; 2, 360 min.

PNA-K⁺ at 467 nm (30 500) in Me₂SO). There was no appearance of a spectral absorption in the 330-nm region in this system but, after long reaction times (20 h), a very small absorption appeared at 654 nm.

Discussion

Identification of Spectral Species and the Reaction Sequence.

It is apparent from the description of the spectral behavior observed in the various PNT-base systems, as given in the Results section, that a sequence of events is indicated by the consecutive appearance and disappearance of a number of spectral absorptions. Thus the assignment of species to these absorptions presents a challenging task. The variation in the spectra among the basic systems appears at first somewhat perplexing but further scrutiny reveals some common features. Especially pertinent is the observation, common to the KH/crown, TPM-K⁺ and dimsyl basic systems, of an initial absorption maximum occurring between 430 and 450 nm. This peak then gradually decreases in intensity and is replaced by a shorter wavelength peak occurring at ~330 nm in the KH/crown and TPM⁻ systems, though this peak is obscured in the case of the dimsyl anion system. The 450-nm absorption is also found in the Fl-K⁺/Me₂SO system, but this time its initial development can be observed as well as its subsequent decline. These two peaks, appearing at ~330 and 440 nm, will receive our attention first, in the task of species assignment.

As stated in the introduction, the only previous UV-vis spectral study of the PNT-base reaction is the brief report by Miller and Pobiner for the *tert*-butoxide-*tert*-butyl alcohol system.²² These workers observed a rapid initial formation of an absorption at 362 nm followed by the consecutive development of peaks at 557 (0.5 h), 300-310 (1-2 h), 538 (3-4 h) and finally 517 nm (24 h). These spectral absorptions were assigned respectively to the *p*-nitrobenzyl anion, a charge-transfer complex, and free-radical species. The charge-transfer

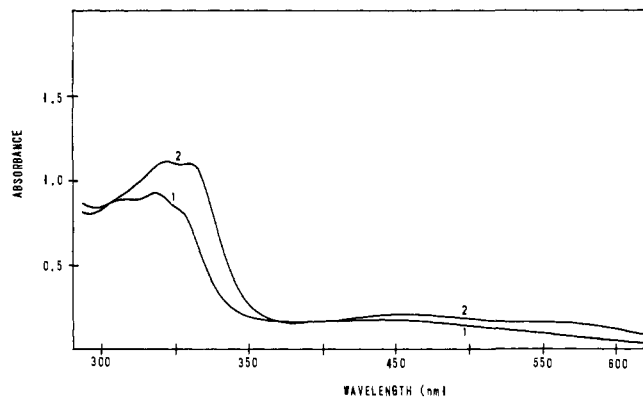


Figure 8. Absorption spectra of *p*-toluene radical anion in DME (spectrum 1) and in DME/18-crown-6 (spectrum 2).

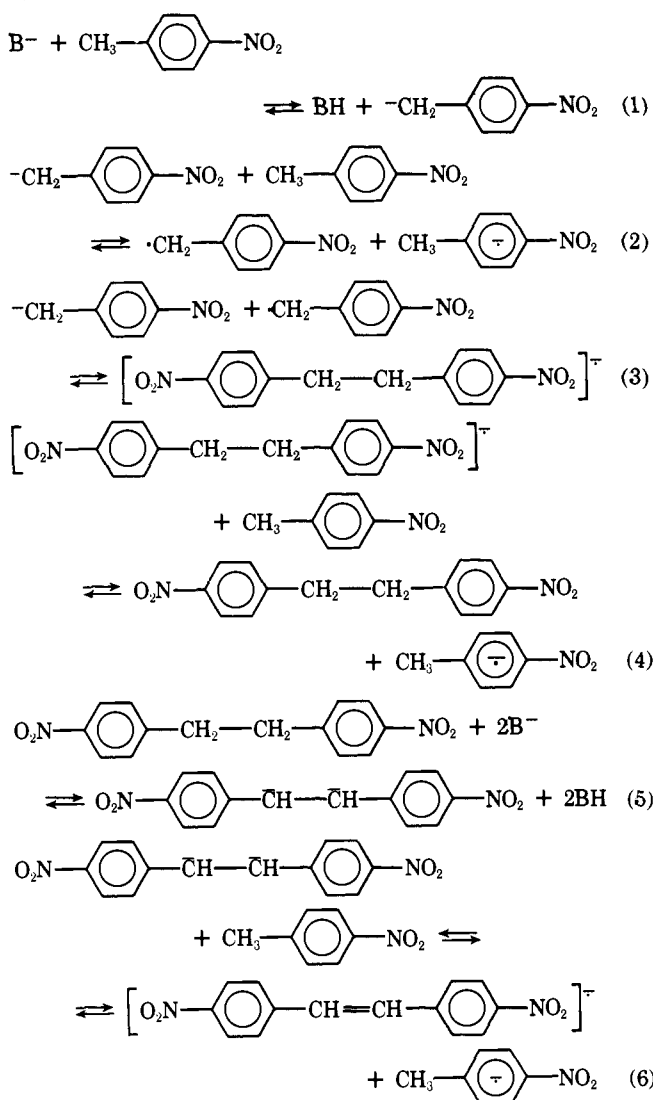
complex was thought to be probably a dimer formed between PNT⁻ and PNT, while the free-radical species were not identified. It was thought that "the intermediate steps between those given are more complex than indicated by Russell and Janzen¹⁴ and cannot be deduced from the data presently available".²²

Thus the only spectral absorption which received definite assignment by Miller and Pobiner was the 362-nm absorption as corresponding to PNT⁻. In our own work a 362-nm absorption was not observed but the ~330-nm absorption could perhaps be thought sufficiently close to correspond to PNT⁻, noting the different solvents used in the two studies. We believe, however, that this assignment would be incorrect. We propose, instead, that the 430-450-nm absorption observed in our work is due to the PNT⁻ anion and that the ~330-nm absorption is due to the PNT⁻ radical anion. This proposal is made in part on the basis of an ESR experiment which was performed for the PNT/KH/crown/DME system and which showed a signal *increasing* in intensity during the first 2 h after preparation of the sample. Monitoring the UV-vis spectrum in parallel showed that during this period the 327-nm absorption was increasing while the 428-nm absorption was decreasing in intensity.

We have obtained independent evidence concerning the UV spectrum of the PNT⁻ radical anion. This species was generated by the action of biphenylpotassium radical anion²⁴ on PNT in DME solvent and found to have a strong band at 316 nm with shoulders at 308 and 325 nm and a weak, broad band centered at ~450 nm (Figure 8). Addition of 18-crown-6 ether resulted in sharpening of the spectrum as seen in Figure 8. Replicate experiments showed that the low-wavelength absorption was sensitive regarding its sharpness and apparent multiplicity, with respect to the presence of crown ether as well as a function of the concentration of PNT⁻. One can reasonably conclude from these spectra of authentic PNT⁻ that the ~330-nm absorption observed in the PNT-base systems described above can also be assigned to the PNT⁻ radical anion.

Some supporting evidence exists concerning the assignment of the ~330-nm absorption in our reaction system to the PNT⁻ radical anion. Thus Shida and Iwata have generated PNT⁻ through γ -irradiation of glassy solutions of PNT in 2-methyltetrahydrofuran frozen at 77 K.²⁵ The UV-vis spectrum of PNT⁻ thus produced showed a strong absorption (ϵ 17 000) centered at 334 nm but split into two subpeaks, λ_{\max} 325 and 343 nm, and a much weaker absorption (ϵ 3500) at 477 nm. The better resolution of the lower wavelength band in the low-temperature glassy state is to be expected, compared to the present results obtained in solution at ambient temperature. The long-wavelength weak absorption would be partially obscured in the PNT-base systems, though a hint of such an absorption is in fact present in the spectrum in Figure 1.

Scheme I



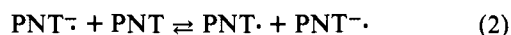
Having assigned the ~ 330 -nm absorption to the PNT^- species, we can now proceed to the 430–450-nm absorption, which, it is recalled, is the *first* formed absorption in the PNT -base systems. We propose that the latter absorption be assigned to the *p*-nitrobenzyl anion. As has been pointed out,^{1b} one can reasonably predict that PNT^- should have its absorption maximum in the 430–450-nm region, on the basis that the benzyl anion has λ_{max} at ~ 360 nm and that introduction of a *p*-nitro group results in a bathochromic shift of ~ 80 nm in related carbanion systems. Moreover, it is also reasonable that this absorption would occur at longer wavelength in Me_2SO medium (i.e., 450 nm) than in THF or DME medium (i.e., 430 nm) since in Me_2SO one would expect to have the free PNT^- anion present, whereas in THF or DME contact or externally crown complexed ion pairs could prevail and these are known to absorb at shorter wavelength relative to the free anions.²⁶

A plausible scheme showing the sequence of events in the interaction of PNT with base is that given in Scheme I, which is analogous to the reaction mechanism proposed earlier by Russell and Janzen.^{15,27} The initial process in this scheme is proton abstraction by base to give PNT^- (eq 1), which is followed by electron transfer from PNT^- to PNT , acting as electron acceptor, to give $\text{PNT}^{\cdot-}$ and PNT^{\cdot} (eq 2). This sequence, eq 1 and 2, requires that the initially observed spectral species be PNT^- , followed by the appearance of $\text{PNT}^{\cdot-}$. The spectral observations (see figures) and our assignment of the respective absorptions are in accord with these conclusions.

The double absorption at 580 and 628 nm formed as the eventual product in the $\text{PNT}/\text{KH}/\text{crown}/\text{DME}$ or $\text{PNT}/\text{TPMK}/\text{crown}/\text{DME}$ systems (Figures 1 and 3) can be assigned to the *p,p'*-dinitrostilbene radical anion, $\text{DNS}^{\cdot-}$. Thus, when authentic *p,p'*-dinitrostilbene (DNS) in DME was treated with potassium in the presence of 18-crown-6 ether, a simple spectral change was observed, the 406-nm absorption due to the reactant gradually decreasing in intensity and a double absorption at 580 and 627 nm, with the latter peak more intense, correspondingly increasing in intensity. The occurrence in the $\text{PNT}/\text{TPM}^-\text{K}^+/\text{Me}_2\text{SO}$ system of the long-wavelength maxima at 630 and 650 nm can presumably be ascribed to a medium effect on the $\text{DNS}^{\cdot-}$ absorption. Shida and Iwata²⁵ also generated $\text{DNS}^{\cdot-}$ in glassy solutions at 77 K through γ -irradiation and recorded a double absorption at 524 and 587 nm, the latter the more intense. It is not clear to us whether the shift to longer wavelength observed in our work should be ascribed to differences in the nature of anion/cation interactions, including complexation, or whether it is the result of the change from the frozen to the solution state. It is reasonable, however, that the highly conjugated $\text{DNS}^{\cdot-}$ system should be more strongly sensitive to such effects relative to $\text{PNT}^{\cdot-}$, in which case the spectral variation was less pronounced.

Proton Transfer vs. Electron Transfer. We have shown that the *p*-nitrotoluene-base systems investigated herein involve the formation of the *p*-nitrobenzyl anion (PNT^-) as well as the *p*-nitrotoluene radical anion ($\text{PNT}^{\cdot-}$). Evidently both proton-transfer and electron-transfer processes are operative and we must inquire into their mechanism as well as sequence in the overall scheme.

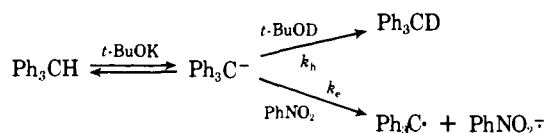
The *p*-nitrobenzyl anion can logically be derived only by proton transfer from PNT to base, as given in eq. 1. The *p*-nitrotoluene radical anion, however, can form by two routes: electron transfer from base to PNT , as given in eq 7, or electron transfer from *p*-nitrobenzyl anion (formed via reaction 1) to PNT yielding the *p*-nitrobenzyl radical (PNT^{\cdot}) in addition to $\text{PNT}^{\cdot-}$, eq 2:



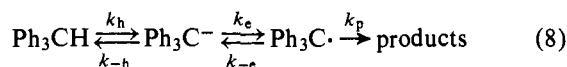
The dilemma posed by the results is that electron-transfer processes are known to be generally fast, whereas proton-transfer processes can often be slow, particularly when, as in the present case, carbon acids are concerned. Hence, in considering reactions 1 and 7, one might have expected electron transfer to be competitive with proton transfer and to lead to the preferential formation of $\text{PNT}^{\cdot-}$. Instead, as we have seen, the present systems are characterized by the initial formation of PNT^- and it is only with the decay of this species that $\text{PNT}^{\cdot-}$ makes its appearance.

Some pertinent studies of competitive electron-transfer and proton-transfer processes have been reported by Guthrie and co-workers.^{28–31} Thus triphenylmethide anion, obtained by action of *tert*-butoxide ion on triphenylmethane, can be efficiently trapped by nitrobenzene acting as an electron acceptor, in competition with protonation by solvent *t*-BuOD (Scheme II). The experimentally observed rate constant ratio, $k_e/k_h \sim 10$, when corrected for the difference in effective concentrations of the two trapping agents, leads to a corrected second-order rate ratio of ~ 400 in favor of electron transfer.

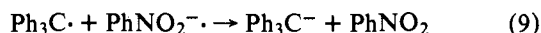
Scheme II



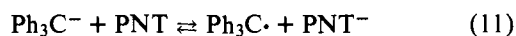
However, this ratio is dependent on the nature of the medium and the counterion, and is, for example, diminished by addition of hexamethylphosphoric triamide (HMPA) or crown ether. It was concluded that ion pairing has a differential enhancing effect on the electron-transfer process relative to proton transfer. Another important conclusion of Guthrie's studies was that the electron-transfer process can be reversible (*vide infra*), so that a more accurate description of the processes in Scheme II is that given by the equation



The additional term k_{-e} refers to the process in eq 9 while k_p includes a number of product-forming steps.



The studies by Guthrie outlined above provide analogies but also contrast with respect to the present work. Considering first the $\text{Ph}_3\text{C}^-/\text{PNT}$ system, the processes in eq 1 and 7 with $\text{B}^- = \text{Ph}_3\text{C}^-$ are in principle analogous to those in Scheme II. However, in the present system Ph_3C^- reacts with PNT concurrently by both electron transfer and proton transfer, unlike Scheme II where these two roles are served respectively by PhNO_2 and *t*-BuOD. It is thus instructive to consider the feasibility of reactions 1 and 7 for the specific case of Ph_3C^- , *i.e.*



One can make a reasonable prediction concerning proton transfer between Ph_3C^- and PNT, in relation to the corresponding process in the $\text{Ph}_3\text{C}^-/t\text{-BuOH}$ system. The $\text{p}K_a$ s of PNT and *t*-BuOH are of the same order of magnitude^{32a} but as acids they differ importantly in that the former is a carbon acid while the latter is an oxygen acid.³⁴⁻³⁶ Now the protonation of Ph_3C^- by *t*-BuOH has been estimated to have a rate constant of $10^7\text{--}10^8 \text{ M}^{-1} \text{ s}^{-1}$, and reaction 10 is hence expected to proceed considerably slower. The effect of changing the medium from *t*-BuOH to media as diverse as THF, DME, or Me_2SO used in the present work is difficult to estimate owing to the many factors involved.³⁷ Hence a value of $10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the forward reaction in eq 10 will be assumed in the subsequent discussion.

Proceeding to the electron-transfer process in eq 11, this is in fact analogous to electron transfer between Ph_3C^- and PhNO_2 shown in Scheme II. The half-wave reduction potentials of PNT and PhNO_2 are quite comparable (-1.20 and -1.15 , respectively, vs. SCE, saturated calomel electrode³⁸). Since the oxidation potential of Ph_3C^- is known to be -1.4 V (vs. SCE),^{39a} one can calculate that the process of eq 11 is thermodynamically favorable to the extent of 0.2 V . Electron transfer between Ph_3C^- and PhNO_2 has been estimated to occur with a rate constant of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in *t*-BuOH,²⁸ and this provides a rough guide for the $\text{Ph}_3\text{C}^-/\text{PNT}$ system as well, with due regard to the uncertainty associated with change in the reaction medium.

The above discussion leads to the conclusion that the electron-transfer process for reaction 11 should occur appreciably *faster* in the forward direction than the proton-transfer process of reaction 10. As has been stated, the dilemma of the present work is that the experimentally observed result appears to be the reverse as far as the order of appearance of species is concerned.

We believe that the observed preferential formation of PNT^- can be explained on the basis of the essential irreversibility of reaction 10 while reaction 11 is effectively reversible. For reaction 10, $\Delta\text{p}K \sim 10$, and the process is greatly favored thermodynamically in the forward direction. If one estimates

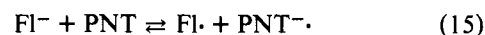
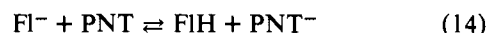
the rate constant for reaction 10 in the forward direction as $10^5 \text{ M}^{-1} \text{ s}^{-1}$ (*vide supra*), then the reverse process would have an associated rate constant of $\sim 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$, *i.e.*, relatively slow. For reaction 11, use of the above oxidation-potential values leads to an equilibrium constant of $\sim 10^3$. If the rate constant for the forward process is taken as $\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$,²⁸ one obtains for the reverse process a rate constant of $\sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$; *i.e.*, the equilibrium is rapidly established. It follows from the above analysis that PNT^- but not $\text{PNT}\cdot$ will be the initial predominant species in the $\text{Ph}_3\text{C}^-/\text{PNT}$ system.

Proceeding to the KH/PNT system, the reactions under consideration, corresponding to the general processes in eq 1 and 7, are



Using a $\text{p}K_a$ value for H_2 of 36 ,²⁰ one obtains an equilibrium constant of 10^{16} for the proton-transfer reaction (12). Hence this reaction is greatly favored thermodynamically in the forward direction. If the rate constant for reaction 12 in the forward direction is taken as $\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, then the reverse process would have a rate constant of $\sim 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$. On the other hand, for the electron-transfer reaction (13), use of the oxidation potential of H^- (-2.25 V in aqueous solution⁴²) and the reduction potential of PNT (-1.2 V) leads to an equilibrium constant of $\sim 10^{17}$. If the rate constant for the forward process is taken as $\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ as previously, one obtains for the reverse process a rate constant of $\sim 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$. Thus these calculations predict that, unlike the $\text{Ph}_3\text{C}^-/\text{PNT}$ system, the electron-transfer reaction (13) should be relatively irreversible. Since the experimental results show that PNT^- is the species initially formed, this would suggest that in the present system reaction 13 is actually reversible. We feel that this is plausible since these reactions are carried out in a polar solvent (Me_2SO) or in an ethereal solvent containing crown ether, and Guthrie²⁸ has shown that under such conditions the electron-transfer reaction between Ph_3C^- and PhNO_2 becomes reversible, unlike the case in nonpolar solvents and in the absence of crown ether.

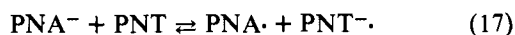
The Fl^-/PNT reaction system is characterized by proton transfer, reaction 14, and electron transfer, reaction 15, that



are relatively inefficient. For reaction 14 the equilibrium constant is estimated as 10^2 , based on the relative $\text{p}K_a$ s of PNT and FIH ($\text{p}K_a = 22.6$ ⁴³). For the electron-transfer reaction (15), an equilibrium constant of ~ 0.5 is calculated from the oxidation potential of Fl^- (-1.18 V ⁴¹) and the reduction potential of PNT (-1.2 V). Thus these calculations predict that the proton-transfer reaction would occur in preference to electron transfer. Additionally, one would expect the rate of proton transfer to be relatively slow, compared with the previous systems considered, since the $\text{p}K_a$ difference between the base and the PNT is now smaller. Both these predictions are borne out by the experimental results.

For the PNA^-/PNT reaction system, the proton-transfer reaction (16) has an equilibrium constant of ~ 2.5 , as calculated from the relative acidities of PNA ($\text{p}K_a = 20.9$ ^{32b}) and of PNT. The equilibrium constant of reaction 17 is estimated as 1.5×10^{-2} from the oxidation potential of PNA^- (-1.09) and the reduction potential of PNT. The oxidation potential of PNA is obtained by extrapolation of oxidation-potential values for similar carbanions as compiled by Kern and Federlin.⁴¹ Thus these calculations predict that the proton-transfer reaction (16) and the electron-transfer reaction (17) are both thermodynamically unfavorable. This is in agreement

with the experimental observations which showed an extremely slow reaction (see Results section).



The $\text{CH}_3\text{SOCH}_2^-/\text{PNT}$ basic system has not been discussed so far. However, the above treatment cannot be quantitatively extended to this system, since the pertinent numerical data are not known. Nevertheless, a qualitative reasoning would suggest that the behavior in this case should be intermediate between that in the $\text{Ph}_3\text{C}^-/\text{PNT}$ and H^-/PNT systems, which is in accord with the observations.

In conclusion of this discussion, we have shown that, in the competition between reactions 1 and 7, PNT^- formation will predominate in all the basic systems examined. It follows that PNT^- formation will thus be controlled by reaction 2, and that this in turn will be limited by reaction 1. All our results are in accord with this scheme.

Comparison with Literature Data. Two studies have appeared in the recent literature concerning the *p*-nitrotoluene-base system, namely, by Miller and Pobiner²² and by Russell and Janzen.¹⁵ UV-visible spectra were obtained only in the former study and, as stated earlier, their assignment is at variance with the present work. However, the base used by Miller and Pobiner,²² viz., *t*-BuOK/*t*-BuOH, differs from those used in the present work and it is pertinent therefore to consider the feasibility of the processes which can occur in the various PNT -base systems.

The primary reactions between PNT and base which lead to proton transfer and electron transfer, as given in eq 1 and 7, are rewritten for the *tert*-butoxide case:



Of these processes, reaction 19 in the forward direction can virtually be eliminated as a possibility since it is thermodynamically extremely unfavorable. Though the oxidation potential of *t*-BuO \cdot in solution has not been reported, the electron affinity of *t*-BuO \cdot in the gas phase has been determined as 1.93 eV,⁴⁴ which is in close agreement with the value of -1.8 eV for the oxidation potential of HO $^-$ in solution.⁴⁵ Accepting this value within the limits of approximation of the present requirement, and recalling that the reduction potential of PNT is -1.2 V, it follows that reaction 13 is unfavorable thermodynamically to the extent of -3.1 eV.

Since formation of PNT^- via reaction 19 can thus be eliminated, then the most likely remaining route for formation of this species is via reaction 2. This makes formation of PNT^- dependent on PNT^- , itself formed via reaction 18. Thus, consideration of the latter process comes next under our scrutiny.

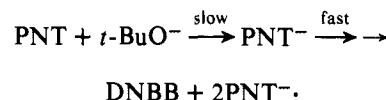
We examine reaction 18 with respect to its equilibrium and kinetic characteristics. The equilibrium process is governed by the relative pK_a s of PNT and of *t*-BuOH, for which literature values of 20.4 (Me_2SO medium) and 19.0 (*t*-BuOH medium), respectively, have been given. Since the reaction under study occurs in *t*-BuOH, a pK_a value for PNT in that medium would be desirable. Literature data suggest that the pK_a s of carbon acids are diminished somewhat in Me_2SO relative to hydroxylic media, but for oxygen acids the reverse holds.⁴⁶ Since PNT^- has negative charge delocalized partly on carbon and partly on oxygen it will be assumed here that the two effects cancel and that the pK_a of PNT will take on the same value in *t*-BuOH as in Me_2SO .

Thus, assuming the pK_a values in *t*-BuOH of 20.5 for PNT and 19.0 for *t*-BuOH, it follows that reaction 18 will have an associated equilibrium constant of 3×10^{-2} at 25 °C. Under

the conditions of Miller and Pobiner's experiments,²² with $[\text{PNT}] = 2.2 \times 10^{-4}$ M and $[t\text{-BuOK}] = 0.2$ M, one calculates $[\text{PNT}^-] = 2.1 \times 10^{-3}$ M, which would correspond to an absorbance value of 31 for a 1-cm cuvette assuming a molar extinction coefficient of $15\,000 \text{ M}^{-1} \text{ cm}^{-1}$ for PNT^- . If our assignment of 440 nm to the PNT^- species is correct, then a strong absorption would be present. A small peak at 440 nm with an absorbance of 0.25 is in fact present initially in the published spectrum but was not remarked upon by Miller and Pobiner.²² However, a clue to the smaller than expected PNT^- concentration in this system is available from the work of Russell and Janzen.¹⁵

The reaction scheme formulated by Russell and Janzen¹⁵ on the basis of an extensive ESR study of the $\text{PNT}/t\text{-BuOK}/t\text{-BuOH}$ system is given in Scheme III.

Scheme III

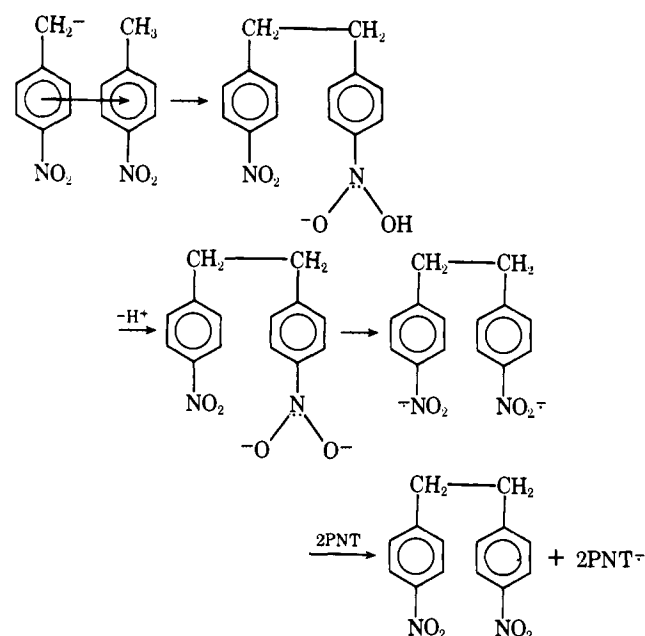


It was pointed out¹⁵ that the observed kinetics in *tert*-butyl alcohol could not be rationalized if an appreciable fraction of the *p*-nitrobenzyl anion is reprotonated, unless this protonation leads to the bibenzyl. This would result in a steady-state concentration of PNT^- that is much below the equilibrium concentration of the anion as calculated above from eq 18. This argument is of course in complete agreement with our evaluation of Miller and Pobiner's work as noted above. It is also in agreement with the conclusions we have drawn at the end of the last section.

On the basis of the above discussion it appears that the principal spectral species present in Miller and Pobiner's study is a charge-transfer complex of the type $[\text{PNT}^- \rightarrow \text{PNT}]$, as proposed previously.¹⁵ This rapidly formed intermediate would then undergo further transformations leading to *p,p'*-dinitrobenzyl (Scheme IV). Further formation of *p,p'*-dinitrostilbene would occur by mechanisms as indicated previously in Scheme I.

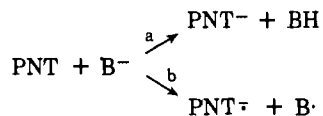
The last step in Scheme IV leading to formation of *p,p'*-dinitrobenzyl will also occur in the presence of other electron scavengers such as molecular oxygen. Such a process would also be possible in the last step of Scheme I leading to formation of the *p,p'*-dinitrostilbene radical anion.

Scheme IV



Conclusions

(1) In the reaction between PNT and the basic systems examined, the major species formed are *p*-nitrobenzyl anion (PNT⁻), *p*-nitrotoluene radical anion (PNT^{-•}), and *p,p'*-dinitrostilbene radical anion (DNS^{-•}). Since the UV-visible spectra of the PNT/base systems show that PNT⁻ is the



first-formed species and following its decay PNT^{-•} is produced, it follows that proton transfer between PNT and base (path a) predominates over electron transfer (path b). DNS^{-•} is formed from *p,p'*-dinitrostilbene in secondary processes.

(2) Formation of PNT^{-•} species in the reaction systems examined has been concluded as mainly the result of electron transfer between PNT and PNT⁻, i.e., PNT + PNT⁻ → PNT^{-•} + PNT.

(3) PNT has been found to react as described under (1) with potassium hydride, triphenylmethylpotassium, dimsylv potassium, and fluorenylpotassium, for which the p*K*_a of the corresponding conjugate acids are greater than that of PNT. Negligible reaction occurs between PNT and potassium *p*-nitroaniline, for which the p*K*_a of the conjugate acid is less than that of PNT.

(4) The course of the reaction, and the nature of species formed, in the present study differs from a UV-visible study reported in the literature²² concerning the reaction between PNT and *tert*-butoxide ion in *tert*-butyl alcohol. However, our results are in general agreement with conclusions drawn from an ESR study reported by Russell and Janzen.¹⁵

Experimental Section

p-Nitrotoluene was recrystallized from ethanol, mp 51.5–52.0 °C. Triphenylmethane (Aldrich) was recrystallized from ethanol, mp 93.5–94 °C. Fluorene (Aldrich) was recrystallized from ethanol, mp 116 °C. *p*-Nitroaniline (Matheson) was recrystallized from aqueous ethanol, mp 147–148 °C. *n*-Butyllithium (Ventron Alfa) was used as a solution (1.8 M) in hexane. Potassium hydride (Ventron Alfa) was obtained as an oil suspension and repeatedly washed with petroleum ether in a drybox under nitrogen prior to use. THF, DME, and Et₂O were distilled from lithium aluminum hydride and stored over *n*-BuLi. Me₂SO was distilled from calcium hydride and stored in evacuated vessels. *p,p'*-Dinitrostilbene was prepared according to published procedure.⁴⁷

The experiments were performed using a reaction vessel consisting of a cylindrical tube (~120 mL) fitted with a 0.1-cm cuvette and adapted for distillation of solvent in vacuo from a reservoir and the introduction of reagents under nitrogen.^{17,20} Following preparation of the reaction solutions, as described below for the series experiments, the vessel was fitted into the modified cell compartment of a Unicam SP800B spectrophotometer and the spectra were recorded intermittently over the range 300–700 nm.

Experiments 1 and 2 were performed by introducing a weighed amount of KH (~0.04 g) into the reaction vessel under nitrogen, evacuating and distilling in DME or THF (~10 mL), followed by addition of PNT (~1–3 mg) in a glass ampule.

In experiments 3 and 4, KH (~0.03 g) and DME (or THF) were introduced into the reaction vessel as in experiments 1 and 2. This was followed by the introduction of a weighed amount of 18-crown-6 (~0.03 g) and, after evacuating, addition of PNT (~2 mg).

For experiment 5, a solution of Ph₃C⁻K⁺ in DME was prepared as follows. KH (~0.03 g), DME (~16 mL), 18-crown-6 (~0.1 g), and Ph₃CH (~2 mg) were introduced into a glass vessel fitted with a Rotaflo stopper and "O"-ring joint.²⁰ After 1 h the solution was filtered under vacuum through a fritted disk into the reaction vessel fitted with a 0.1-cm cuvette, as described previously.²⁰ To the solution of Ph₃C⁻K⁺/18-crown-6/DME, an ampule containing PNT (~2 mg) was added.

A stock solution of dimsylv potassium in Me₂SO (0.017 M) was prepared by introducing a weighed amount of KH (~0.02 g) into a

storage vessel equipped with a Rotaflo stopper and "O"-ring joint.¹⁷ Dry Me₂SO (~20 mL) was transferred under vacuum, as described previously.²⁰ For experiment 6, to the reaction vessel containing Ph₃CH (~4 mg) in Me₂SO (~30 mL) was added under vacuum a sufficient quantity of the stock solution of dimsylv potassium in Me₂SO (0.017 M) until the Ph₃CH was partially converted into Ph₃C⁻K⁺ as shown spectrophotometrically and to this solution was added PNT (~3 mg).

In experiment 7, a solution of dimsylv potassium in Me₂SO was prepared in the reaction vessel from KH (~0.03 g) and Me₂SO (~20 mL) and to this was added PNT (~2–3 mg).

In experiment 8, to the reaction vessel containing fluorene (~6 mg) in Me₂SO (~16 mL) under vacuum was added the stock solution of dimsylv potassium in Me₂SO (0.017 M), until the fluorene was partially converted to Fl⁻K⁺ as indicated by spectral measurements. A weighed quantity of PNT (~4 mg) was then added.

In experiment 9, to the reaction vessel containing *p*-nitroaniline (~2 mg) in Me₂SO (~13 mL) was added a stock solution of dimsylv potassium in Me₂SO (0.017 M) until absorption measurements showed partial conversion to PNA⁻K⁺, and PNT (~2 mg) was then added.

Potassium biphenyl solution was prepared by reacting a solution of biphenyl in DME (0.15 M) with potassium (0.5 g). For the preparation of PNT^{-•}, the stock solution of potassium biphenyl was diluted with DME in the reaction vessel and its concentration determined spectrophotometrically, using the extinction coefficients reported for sodium biphenyl.²⁴ To this solution was added a weighed quantity of PNT (~1 mg).

4,4'-Dinitrostilbene radical anion was generated as follows. To the reaction vessel fitted with a 1-cm cuvette was added 4,4'-DNS (~0.5 mg), followed by distillation of DME (~17 mL). Potassium (~0.05 g) was then introduced, followed by 18-crown-6 (~2 mg), at which point the solution changed color to green.

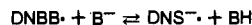
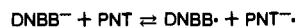
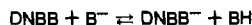
For the ESR measurements the reaction vessel was fitted with a 0.1-cm quartz cuvette as well as a glass tube of 1–3-mm diameter and the solution prepared as in experiments 3 and 4. After some of the solution was transferred into the glass tube, it was sealed and examined on a Bruker ER-420 spectrometer with a Varian field dial and 9-in magnet system. The remaining solution in the reaction vessel was simultaneously scanned spectrophotometrically in the usual way.

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 (27) As an alternative continuation of the sequence in Scheme 1, reaction 4 could be followed by



This reaction sequence would avoid the formation of the dianionic species DNBB^{2-} in eq 5. We hope to be able to differentiate between these possibilities in future work.

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Aromatic Substitution. 45.¹ Transfer Nitration of Aromatics with *N*-Nitropyridinium and Quinolinium Ions

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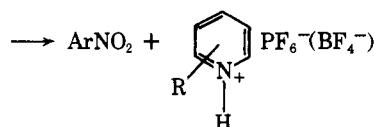
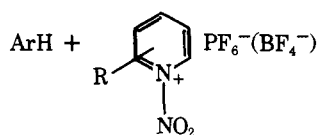
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Abstract: The transfer nitration of aromatics with various *N*-nitropyridinium and quinolinium salts (PF_6^- or BF_4^-) was studied. The nitrations were found to take place via a nucleophilic displacement pathway, involving the *N*-nitropyridinium ions themselves and not free nitronium ion. Steric factors were, however, shown to play an insignificant role in determining the positional selectivity of nitration. Positional and substrate selectivities were found to be independent of one another and are suggested to be determined in two separate steps.

Introduction

Electrophilic aromatic nitration is usually carried out with nitric acid, generally in the presence of sulfuric acid.² Nitration can also be effected with alkyl or metal nitrates, catalyzed by Lewis or Brønsted acids.²⁻⁵ Acyl and aroyl nitrates are capable of nitrating aromatics in the absence of catalysts.⁵ These nitrating agents can be considered to be precursors of the nitronium ion and nitrate aromatics in displacement-type reactions.

We report now on the transfer nitration of aromatics with *N*-nitropyridinium and *N*-nitroquinolinium salts.



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Nitrations with these salts can be carried out under essentially neutral conditions, because the only acid present, due to proton elimination from the nitration of aromatics, will bind with the liberated heterocyclic base. At the same time, the reactivity of the nitrating agent can be varied by altering the electron demand as well as the steric crowding of the heterocyclic ring with suitable substituents.

In 1968, Olah and Olah⁷ first reported on transfer nitration with *N*-nitropyridinium tetrafluoroborate, primarily of *n*-donor substrates. Cupas and Pearson⁸ subsequently, in a preliminary communication, extended the work to substituted *N*-nitropyridinium salts, which were found capable of nitrating aromatics. In continuation of our joint interest, we herein report in full extended studies on the transfer nitration of aromatics with *N*-nitropyridinium and *N*-nitroquinolinium salts.

Results and Discussion

N-Nitropyridinium and *N*-nitroquinolinium salts were prepared by the method of Olah and Olah.⁷ Dropwise addition of the corresponding pyridine derivative to an equivalent amount of the nitronium salt in acetonitrile, nitromethane, or sulfolane solution gives the corresponding *N*-nitropyridinium ions in practically quantitative yield. The salts were studied