to an adduct of the $C_2H_5SO_2$ radical with the trap. From this it was concluded that breakdown of (IV) under photolysis is exclusively by mechanism (1a).

Although the presence of peroxides is known to promote the breakdown of the alkanesulfochlorides [8], there is no agreement as to which of the sulfochloride bonds it is that is attacked by the radicals resulting from peroxide decomposition. Study was therefore made of the breakdown of (IV) under the action of acetyl peroxide in the presence of MNP. Figure 2 shows that the spectrum obtained here contained the triplet with $a_{\rm N} = 12.2$ Oe and a triplet of doublets ($a_{\rm N} = 6.9$ and $a_{\rm H} = 1.5$ Oe), the latter ascribed to an adduct of the CH₃CHSO₂Cl radical with MNP (Exp. Nos. 14, 15). Thus the CH₃ radicals formed in the photolysis of acetyl peroxide can detach either a Cl atom or a CH₂ group H atom from the molecule of (IV).

EXPERIMENTAL

The experimental methods followed here have already been described in [9]. The concentrations of the sulfohalide solutions in benzene ranged from 1.5 to 3 moles/liter. The tert-butyl peroxide -triethylsilane system was used to initiate reaction, the concentrations being TBP, 0.8 and Et_3SiH , 2.4 moles/liter. The concentration of acetyl peroxide when used as an initiator was fixed at 2 moles/liter.

CONCLUSIONS

Electron spin resonance studies using 2-methyl-2-nitrosopropane and phenyl-tert-butylnitron as spin traps have been carried out on the homolytic breakdown of ethanesulfochloride, sulfuryl chloride, sulfuryl fluorochloride and benzosulfohalides of the form $PhSO_2X$ (X = Cl, F, Br).

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CHEMICAL POLARIZATION OF NUCLEI IN REACTIONS

OF AZO COMPOUNDS

1. ¹H AND ¹³C CPN EFFECTS IN THE THERMOLYSIS OF TRIAZENES

IN STRONG MAGNETIC FIELDS

A. V. Dushkin, I. M. Sycheva,T. V. Leshina, R. Z. Sagdeev,and A. I. Rezvukhin

UDC 543.422.25:541.515:547.236.2:541.139

The triazenes, compounds of the type R_1 $N-N=N-R^3$, are among the most widely used sources of free license in organic chemistry. In bread outline the mechanism of radical breakdown of these compounds has

radicals in organic chemistry. In broad outline the mechanism of radical breakdown of these compounds has been satisfactorily established by chemical methods [1, 2].

Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 553-558, March 1977. Original article submitted January 15, 1976.

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	}	¹ H CPN products			
Triazene	Solvent (T, °C)	within the cage	outside the cage		
Methylphenyltriazene (MPhT)	n-Decane, hexaethyldi- siloxane (HEDS), nitro-	C ₆ H ₅ NHCH ₃	o-CH ₃ C ₆ H ₄ NO ₂		
(benzene, 1,1,2,2-tetra- chloroethane (120-130)	Ε	$\frac{CH_4}{A}$		
Ethylphenyltriazene (EPhT)	n-Decane, 1, 1, 2, 2-tetra- chloroethane (110)	$C_6H_5NHCH_2CH_3$ E E/A	$\frac{C_2H_6}{F}$		
tert-Butylphenyltria- zene (BuPhT)	1,1,2,2-Tetrachloro- ethane (110)	$C_6H_5NHC(CH_3)_3$	$H_2C = C (CH_3)_2 E$ $HC(CH_3)_3 E, E/A$		
Benzylphenyltriazene (BPhT)	n-Decane, HEDS (120)	$C_6H_5NHCH_2C_6H_5$ E	$(C_6H_5CH_2)_2 A$ $C_6H_5CH_3$		
Diphenyltriazene	HEDS (180-200)	$(C_6H_5)_2NH$	$\underline{C_6H_5}NH_2 o, p = E$		
(DPIII)		A	$\begin{array}{c} m=A\\ C_6H_6E \end{array}$		
Triphenyltriazene (TPhT)	HEDS (180-200)	$(C_6H_5)_3N$	$\begin{array}{c} C_{6}H_{6}E\\ (C_{6}H_{5})_{2}NH \end{array}$		
Diethylphenyltria-	HEDS (230)	$C_6H_5N(CH_2CH_3)_2$	(CH ₃ CH ₂) 2NH		
(Ľ	A		

TABLE 1. ¹H CPN Effects in Triazene Thermolysis

* E designates emission, A absorption, and \mathbb{Z}/A a multiplet effect. Product yields in the thermolysis of MPhT, EPhT, BuPhT, BPhT, and DPhT are given in [2]. Yields in the thermolysis of TPhT and DEPhT have not been determined.

The present work was a study of the chemical polarization of nuclei (CPN) accompanying the thermolysis of various triazenes in strong magnetic fields (Table 1). The aim was to obtain additional information concerning radical – reaction product precursor interaction in such systems and, at the same time, develop a detailed mechanism for CPN effects.

Study of CPN effects in triazene systems has been largely limited to the thermolysis of 1,3-diphenyltriazene (DPhT) [3-5]. The mechanism of DPhT decomposition can, according to [1, 2], be described by the following reaction scheme:



This scheme is consistent with data applying to 13 C and 15 N CPN effects in this reaction, and with the fact that 14 H CPN effects are observed in benzene and aniline, the reaction products [3, 4].

Detailed study of the thermolysis of DPhT in hexaethyldisiloxane solution at 180 °C showed not only ¹H CPN effects in benzene and aniline, but also an integral polarization of the phenyl protons of diphenylamine, the product resulting from cage recombination (cf. Table 1). This would also be consistent with Scheme 1. Unfortunately, the data presently available give no indication as to which of the radical pairs (RP), (1) or (2), is the site of the ¹H CPN effect.* Only benzene polarization is observed in the thermolysis of triphenyltriazene (TPhT), the situation here being different from that met with DPhT.[†] The sign of the benzene CPN effect is also consistent with the requirements of Scheme 1. Diphenylamine is not polarized in this reaction, obviously because of the high stability of the diphenylazo radical ($T_{1 Nu}^{R} < \tau_{R}$).[‡]

*The attempt was made to clear up this point by studying the ¹H CPN effect in the benzene resulting from the weak magnetic field reaction. The sign of the CPN, and the value of the coefficient showing the amplification of the CPN effect with increasing magnetic field strength, were such as to suggest the RP-2 as the principal site of ¹H polarization.

[†]The PMR spectrum gave no indication of triphenylamine formation in this reaction.

 $\ddagger T_{1Nu}^{R}$ is the time required for spin-lattice relaxation of the radical nucleus, τ_{R} the precombination lifetime of the radical R.

Carbon atom	4 - CH2-NH 2'		42CH224		4 <u>2</u> -NH2	
	ô, ppm	CPN	ø, ppm	CPN	ð, ppm	CPN
CH ₂ C-1 C-2 C-3 C-4 C-1' C-2' C-3' C-4'	48,4 140,3 127,6 127,6 127,2 158,2 113,6 127,2 118,0	$\begin{vmatrix} A, E/A \\ E \\ - \\ - \\ A, E/A \\ A \\ E, E/A \\ A, E/A \\ E, E/A \end{vmatrix}$	38,2 141,9 128,6 128,6 128,6 126,0	A/E A _ _	146,7 (115,4 128,0 118,8	E A, A/E E, A/E A, A/E

TABLE 2. 13 C CPN Effects in the Thermolysis of Benzylphenyl-triazene in n-Decane

The mechanism of aliphatic – aromatic triazene thermolysis has also been largely developed from study of the thermolysis products [2]. This mechanism can be represented by the following scheme:

$$C_{6}H_{5}NH-N=NR \rightarrow \overline{C_{6}H_{5}NH \cdot R} \xrightarrow{S} \rightarrow C_{6}H_{5}NHR$$

$$\downarrow^{(3)}$$

$$RH, C_{6}H_{5}NH_{2} \xleftarrow{Solvent} C_{6}H_{5}NH \cdot , R \cdot \rightarrow \overline{C_{6}H_{5}NH \cdot R} \xrightarrow{F}$$

$$R-R, R(-H), RH \leftarrow \overline{R \cdot R} \xrightarrow{F}$$

$$Scheme 2$$

Study of Scheme 2 suggested the presence of products from the recombination and disproportionation of RP's with uncorrelated spins (F pairs), the situation here being different from that met with the aromatic triazenes. The products from such pair recombination are indicated by R-R and R(-H), RH in Scheme 2. The analysis of the ¹H and ¹³C CPN effects summarized in Tables 1 and 2 was aimed at estimating the relative contributions of the S and F pairs to the total polarization of products obtained from the thermolysis of various triazenes. Analysis of the ¹H CPN effect in the N-alkylanilines resulting from thermolysis of MPhT, BPhT, and EPhT (cf. Table 1) indicated that these compounds are largely products from cage recombination of the singlet RP (3) pairs: $\overline{C_{eH_5}NH..R^S}$.

Because of the high activity of the CH_3 and C_2H_5 radicals in detaching H atoms from the solvent, CPN effects in CH_4 and C_2H_6 , the products obtained from reactions outside the cage, also trace back to the RP (3). The fact that the signs of the CPN effects in CH_4 and C_2H_6 are different can be understood by noting the difference in signs of the hyperfine interaction (hfi) constants for the methyl protons in the methyl radicals ($a_{CH_3} < 0$) and ethyl radicals ($a_{CH_3} > 0$, $a_{CH_2} < 0$).* Thermolysis of MPhT in nitrobenzene yields not only CH_3 but also positively polarized o- and p-nitrotoluenes. The fact that the signs of the NCP effects in CH_4 and the nitrotoluenes (CH_3 group) were the same, was taken as indication that the NCP of the latter compounds traces back to the primary singlet RP. It is clear that the pair with uncorrelated spins is the immediate precursor of the reaction products

though it itself does not contribute to CH_3 group CPN. This situation probably reflects the low value of the hfi constant for the CH_3 group protons in the cyclohexadienyl radical [6].

In addition to these effects, intense ¹H CPN signals were observed in the thermolysis of MPhT and EPhT in all solvents, the signs being such as to indicate the presence of products from cage reactions. In the case of MPhT, we have ascribed these signals to the CH₃ group (δ 2.05 ppm, J_{H-CH₂} = 8 Hz) of the product resulting from CH₃ radical introduction into the anil radical ring; in the case of EPhT to the CH₂ group (δ 2.66 ppm, J_{H-CH₂} = 4 Hz), of the product resulting from C₂H₅ radical introduction into the anil radical ring, i.e., to 1-methyl-2-imino-3,5-cyclohexadiene and 1-ethyl-2-imino-3,5-cyclohexadiene. It is also possible that 1-methyl-4-imino-2,5-cyclohexadiene are formed in these reactions.

*The principal contribution to the C_2H_6 polarization comes from the CH_3 protons of the C_2H_5 radical.



Fig. 1. Observed (lower) and calculated (upper) NMR polarization spectra for the CH₂ group of Nethylaniline (a), and 1-ethyl-2imino-3,5-cyclohexadiene (b).



The possibility of the formation of these side products has been discussed in [1], but separations were not undertaken there. Even we have not attempted to carry out such separation, the yields of these products being quite low in each case. Products were identified by comparing experimentally developed polarization spectra with spectra obtained through theoretical calculations (Fig. 1).*

Thermolysis of BuPhT and BPhT leads to the formation of $t-C_4H_9$ and $C_6H_5CH_2$ radicals which show low activity in the detachment of hydrogen atoms and disappear from solution largely as a result of recombination and disproportionation [2]. Here one should anticipate CPN effects in RP with uncorrelated spins. An analysis based on the Kaptein rule showed the CPN effect in isobutane to be a superposition of an integral polarization in the RP (3) (cf. Scheme 2) and an a multiplet effect in the F pair consisting of two $t-C_4H_9$ radicals.

It is possible that N-alkylaniline formation in the BuPhT and BPhT reactions proceeds through either the RP (3) or the F pair (4). The result is to reduce the values of the polarization coefficients of N-tert-butyl- and

^{*}The NMR polarization spectra were calculated by the methods of [6]. The relative populations of the nuclear spin states were obtained from the exponential model, assuming J = 0 [6]. The frequencies and transition probabilities of [7] were used in developing the NMR spectra of the A_2B_3 and A_2B_3X spin systems. The NMR multiplet polarization spectra were obtained by multiplying the nucleus spin state populations by the corresponding transition probabilities.

N-benzylanilines in comparison with the values for the N-methyl- and N-ethylanilines, the CPN of the S and F pairs being assumed opposite in sign [8]. This last assumption is supported by the fact that addition of excess thiophenol, a hydrogen atom donor, to the thermolyzed BPhT led to an increase in the measured value of the CPN coefficient for N-benzylaniline. Under these conditions, dibenzyl was formed in only insignificant proportions, toluene being the principal product obtained from reaction outside of the cage.

We have also studied the ¹³C CPN effect in the thermolysis of BPhT (cf. Table 2). Experiments with proton suppression showed zero integral polarization of the dibenyl α -hydrogens, with positive polarization of the ¹C atom of the benzene ring. These differences in the sensitivity of the α -hydrogen atoms and the ¹C atom of the dibenzyl ring to integral CPN effects in the RP (3) trace back to differences in the relaxation times of these nuclei in the benzyl radical, where, according to [9, 10]

$$\frac{1}{T_{1\,\text{a-C}}^{R}} \left| \frac{1}{T_{1\,\text{C}}^{R}} = \frac{\rho_{\alpha-\text{C}}^{2}}{\rho_{\text{C}}^{2}} \approx 10 \right|$$

Here the α -¹³C with the shorter T_{1Nu}^R value "forgets" the CPN effect in the primary RP, while the ¹C with the longer T_{1Nu}^R value still remembers it. Monoresonance leads to multiplet (A/E) polarization of the α -carbon atom. It would seem that such an effect could arise only in RP formed from two benzyl radicals, a conclusion supported by theoretical considerations. Thus, analysis of the ¹³C CPN effects in the BPhT thermolysis showed that polarization of dibenzyl is a superposition of effects from S and F pairs, the situation here being similar to that observed with the ¹H NCP effect in the isobutane formed in BuPhT thermolysis.

Comparison of the experimental and theoretical ¹³C spectra for the polarized triplet of the α -CH₂ group of N-benzylaniline made it possible to estimate the difference in g factors of the benzyl and anil radical RP's, the result obtained being $\Delta g = 8 \cdot 10^{-4}$. Knowing the value of g for the benzyl radical to be 2.0026 [11], the value of g for the anil radical, previously unknown, was calculated to be 2.0034.

Reaction scheme 1 for the aromatic triazenes can be used in interpreting the CPN effects observed in the thermolysis of the aliphatic-aromatic triazene DEPhT.

EXPERIMENTAL

The triazenes were synthesized and purified by the methods of [12]. The solvents were cp grade, each purified by distillation. Thermolysis was carried out in the spectrometer detector, working at concentrations in the 0.5-1 mole/liter range. The temperature was held constant to within $\pm 1^{\circ}$ C. The NMR spectra were obtained with JNM-4H-100 and Varian 4-56/60 A spectrometers.

The ¹³C NMR spectra were obtained with a Bruker HX90/8-15 spectrometer working at a frequency of 22.63 MHz with suppression of spin-spin coupling $\{^{13}C-{}^{1}H\}$ and ${}^{13}C$ monoresonance. External stabilization was with respect to the deuterium of D₆-dimethyl sulfoxide. n-Decane served as the internal standard. The pulse interval was 1 sec. Each ${}^{13}C$ NMR spectrum represents 30 superpositions, with recording begun 10 sec after inserting the sample in the spectrometer detector.

The reaction products were identified from NMR spectra obtained by adding various compounds to the reaction mixture.

The authors would like to thank Yu. N. Molin for a discussion of this work.

CONCLUSIONS

1. Thermolysis of doubly substituted aliphatic-aromatic triazenes proceeds through the formation of $\overline{C_{e}H_{5}NH..R}$ S radical pairs (RP) in the initial stages of the reaction (R is an alkyl radical).

2. It is suggested that thermolysis of methyl- and ethylphenyltriazenes leads to the formation of 1-methyl-2-imino-3,5-cyclohexadiene and 1-ethyl-2-imino-3,5-cylcohexadiene, unusual compounds resulting from the recombination of ethyl and methyl radicals with anil radicals.

3. Interference of ¹H and ¹³C CPN effects in the $\overline{C_{6}H_{5}NH..R}^{S}$, $\overline{C_{6}H_{5}NH..R}^{F}$ and $\overline{R..R}^{F}$ RP's was observed in the thermolysis of benzyl- and tert-butylphenyltriazenes.

4. A value has been obtained for the anil radical g factor.

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CHEMICAL POLARIZATION OF NUCLEI IN REACTIONS

OF AZO COMPOUNDS

2. ¹H AND ¹³C CPN EFFECTS IN THE THERMOLYSIS OF TRIAZENES

IN WEAK MAGNETIC FIELDS

A. V. Dushkin, I. M. Sycheva, T. V. Leshina, and R. Z. Sagdeev UDC 543.422.25:541.515:547.236.2:541.139

One of the central problems involved in the treatment of CPN effects in weak magnetic fields is that arising from the electron exchange interaction induced in the radical pair by the polarization process. Theoretical considerations indicate that it should be possible to determine the energy of radical pair (RP) electron exchange interaction in solution from CPN data [1], but definitive information on the role played by such interaction in fixing the weak-field nuclear polarization cannot be obtained in this way.* Values of the exchange integrals for the RP's formed in certain photochemical reactions have been reported in [3, 4]. More recently, however, these same results have been obtained without taking exchange interaction into account, assuming that J = 0.

The present work was a study of weak magnetic field CPN effects in the radiolysis of $\frac{R_1}{R_2}$ NN = NR³ type

triazenes. The aim here was to obtain information concerning exchange interaction in these systems. The radical steps involved in the thermolysis have already been studied in detail by strong field CPN methods [7]. Choice of the particular triazenes was dictated by the fact that RP's of various composition could be readily obtained by correct selection of the substituent R.

The products obtained from the thermolysis of methylphenyl- (I), benzylphenyl- (II), 1,3-diphenyl- (III), and triphenyl- (IV) triazenes proved to be especially suitable for weak-field studies since they had rather long nuclear relaxation times (T_1) and gave clear-cut nonoverlapping polarization signals.

*To date, the only confirmed instances of electron exchange interaction effects are those associated with CPN in biradical reactions.

Institute of Chemical Kinetics and Combustion, Siberian Branch of the Academy of Sciences of the USSR, Novosibirsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 559-563, March, 1977. Original article submitted January 15, 1976.

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