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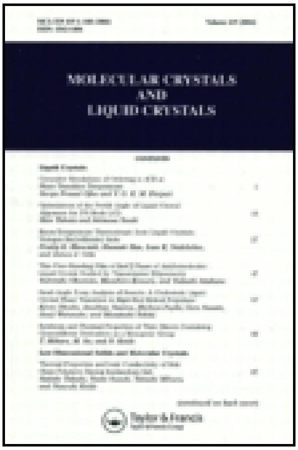

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Paramagnetic Resonance Studies of uv and Thermally Induced Radicals in Trinitrotoluene and Dinitrotoluene

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Paramagnetic Resonance Studies of uv and Thermally Induced Radicals in Trinitrotoluene and Dinitrotoluene

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Electron paramagnetic studies of uv and thermally decomposed 2,4,6 TNT trinitrotoluene (TNT) in the condensed phase show the presence of a triplet spectrum due to an unpaired electron interacting with a nitrogen nucleus. The components of the axially symmetric g and A tensor are; $A_\perp = 4.0$ G, $A_\parallel = 27.0$ G., $g_\perp = 2.007$ and $g_\parallel = 2.003$. When the decomposed TNT is dissolved in benzene a spectrum with the same spin Hamiltonian parameters is obtained but a further hyperfine interaction with five equivalent hydrogen nuclei is observed. Spectra having the same parameters were also observed when 3,4,5 TNT and 3,5 DNT were dissolved in benzene after decomposition. The spectra are assigned to a radical having an unpaired electron localized on an NO group formed by the removal of an O^+ from the NO_2 group of TNT. An irreversible decrease of the isotropic hyperfine splitting with the nitrogen nucleus was observed with increasing temperature in the molten phase of TNT. The possible role of this radical in the thermal initiation of explosion is discussed.

INTRODUCTION

Despite the long history of the use of the phenomena of the initiation of detonation in such molecules as trinitrotoluene there remains little knowledge of the initial chemical steps of the process. Global reaction rates obtained from differential scanning calorimetry experiments are able to predict explosive behavior, such as the critical temperature for

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thermal explosion when used to solve the Frank-Kamenetzky thermal explosion equation.[1] However, the detailed chemical steps that constitute this global rate are unknown. One possibility is that there is a rate controlling step, perhaps the initial step, which dominates and controls the process. The verification of this possibility and the identification of the rate controlling step would be a significant advance in the understanding of the initiation process. It is generally agreed that the initial step is an endothermic scission of the internal molecular bonds of the molecules that make up the explosive followed by an exothermic reaction between the fragments which are quite likely radicals. In fact, recent electron paramagnetic resonance studies of energetic organic materials thermally decomposed in the molten phase indicate the role of radicals in the early stages of the chemistry of initiation.[2,3] Although detailed studies of the kinetics of the formation of these spectra were made, no identification of the radicals giving rise to the spectrum was reported. The purpose of this report is to make a detailed study of the properties of the electron paramagnetic resonance (EPR) spectrum in uv and thermally decomposed 2,4,6, trinitrotoluene (TNT) in order to identify the radicals giving rise to the spectrum. In particular, the spectrum is studied in the solid state where the radicals are fixed in orientation allowing a determination of the principal components of the g and the A tensor. The EPR spectrum of decomposed TNT dissolved in liquid and frozen benzene was also studied. The EPR of 3,4,5 TNT and 3,5 dinitrotoluene dissolved in benzene was also investigated. The temperature dependence and thermal stability of the radical in solid TNT was also studied.

EXPERIMENTAL

Electron paramagnetic resonance measurements were carried out using a Varian E-9 spectrometer operating at 9.2 Ghz. Studies of the effect of temperature on the spectra were made while the sample was in the microwave cavity using a Varian 4540 temperature controller which regulated the temperature to ±1 degree centigrade. Ultra-violet light irradiations of finely powdered samples were made at room temperature using a Hanovia high pressure mercury light of 140 Watt power and peak wavelength 250 nm. All samples of nitrotoluenes used were triply re-crystallized from various organic solutions. No spectra were observed in the unirradiated samples.

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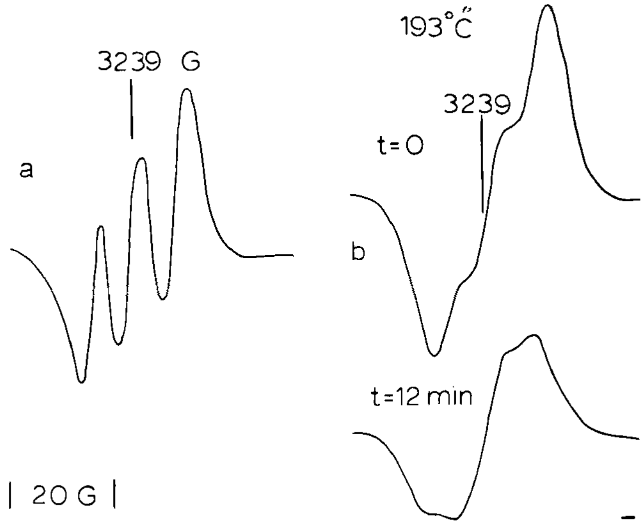

FIGURE 1 (a) EPR spectrum of TNT uv decomposed at room temperature and recorded at 160 °C. (b) Spectrum at 190 °C showing the decay of the outer lines. This spectrum is less well resolved then that in (a) because there is some broadening of the individual lines of the spectrum as the decay occurs.

RESULTS

Powders of 2,4,6 TNT subjected to uv irradiation at room temperature yielded an isotropic triplet spectrum, shown in Figure 1a, when the data were recorded in the liquid phase of TNT above the 89 °C melting point. The spectrum consists of three lines of equal intensity and with equal spacing between the lines. Just above the melting point the separation is 12.0 *G*. As will be discussed below, this decreases as the temperature is raised. The *g* value at the center of the spectrum is 2.005, and is independent of temperature. This spectrum is the result of an unpaired electron having a hyperfine interaction with a nucleus of spin one as a nitrogen nucleus. At very low modulations some evidence of structure was observed on each line of the triplet but was poorly resolved in the molten phase of TNT. Dissolving the decomposed TNT in low concentrations in benzene and recording the spectrum did improve the resolution.

When a molecule or radical is fixed with respect to the dc magnetic field the dipolar anisotropic hyperfine interactions are no longer averaged to zero as in the liquid and the separation of the resonances from each other become dependent on the orientation of the radicals with respect to the applied dc magnetic field. Since a powder is a

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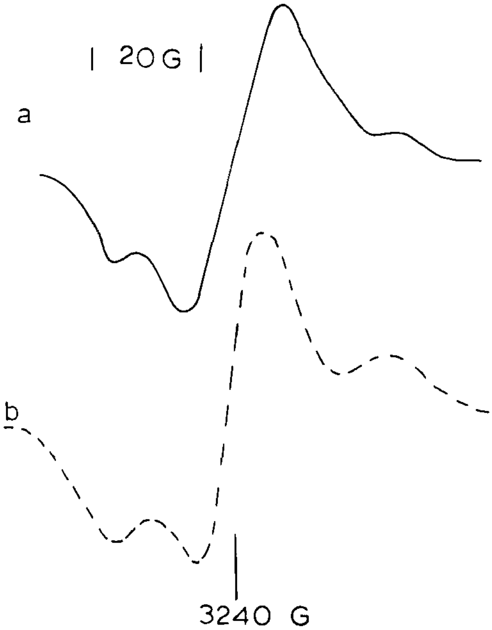

FIGURE 2 (a) EPR spectrum recorded at room temperature in fine powders of TNT which were uv irradiated at room temperature. (b) Computer generated simulated powder spectrum assuming a Gaussian line of 7.0 *G*. width and spin Hamiltonian parameters $A_\perp = 4.0$ *G*., $A_\parallel = 27.0$ *G*., $g_\parallel = 2.003$, and $g_\perp = 2.007$.

collection of randomly oriented single crystals, the fixed axis of the radicals will be randomly oriented. The EPR spectrum in a powder will then consist of a superposition of spectra (weighted by the function which governs the angular dependence of the splittings) arising from all possible orientations. Figure 2a shows the spectrum obtained in powders of TNT uv irradiated at room temperature. If the spectrum arises from the same radical giving rise to the spectrum observed in the melt, the separation of the two outer lines of the powder spectrum should measure $2A_z$, where A_z is the z component of the hyperfine tensor. Since 12.0 *G* is a measure of the isotropic splitting determined in the liquid phase, assuming an axially symmetric hyperfine tensor, the perpendicular component, $A_\perp$, can be obtained from the trace of the hyperfine tensor,

$$A_{iso} = \frac{A_\parallel + 2A_\perp}{3} \tag{1}$$

Assuming the signs of the tensor components are all the same, $A_\perp$ is

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obtained to be 4.0 G, and $A_{\parallel}$ measured directly from the spectrum is 27.0 *G*. In order to verify that the powder spectrum arises from a spectrum with these components a computer simulation of the powder spectrum was made using a program developed by Luckhurst for a 620 L Varian computer. The simulation was made assuming an $S = \frac{1}{2}$ system with $I = 1$, and $A_{\perp} = 4.0$ *G*., $A_{\parallel} = 27.0$ *G*., $g_{\parallel} = 2.003$, and $g_{\perp} = 2.007$. The line shape was taken as Gaussian with a width of 7.0 *G*. The simulation shown in Figure 2b, is in reasonably good agreement with experiment. Note that the trace of the *g* tensor, $(g_{\parallel} + 2g_{\perp})/3$ corresponds to the *g* value at the center of the triplet spectrum measured in the liquid phase as it should if the spectrum in the solid and the liquid are due to the same radical.

The triplet spectrum in the molten phase shows interesting behavior when the temperature is raised above 91 degrees. As the temperature is raised to 160 °C there is a gradual reduction of the isotropic hyperfine interaction from 13.0 *G*. to 7.5 *G*. Figure 3 shows a plot of the isotropic hyperfine interaction as a function of temperature. This decrease in the hyperfine splitting with increasing temperature is not reversible in the sense that the splitting does not return to its original value when the temperature is lowered to 91 degrees.

Above 185 °C the intensity of the two outer lines of the triplet decrease with respect to the intensity of the center line of the spectrum. This effect is shown in Figure 1b. Figure 4 shows a plot of the log of the fractional decrease of the intensity of the outer lines as a function of time at a number of temperatures. The plot shows that the

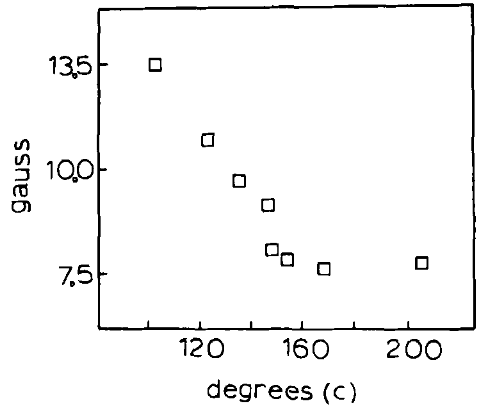

FIGURE 3 Temperature dependence of the isotropic hyperfine splitting of the radical in molten TNT.

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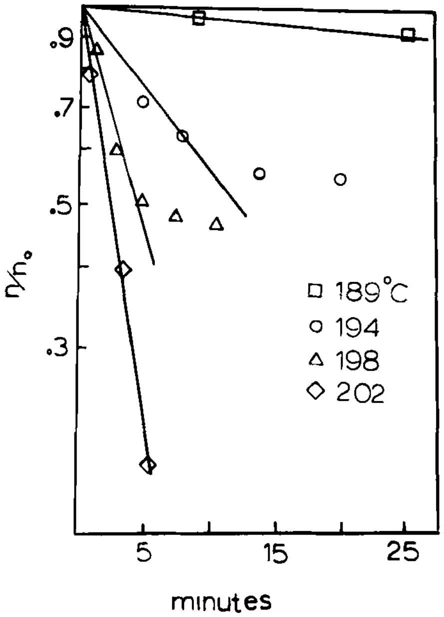

FIGURE 4 Plot of the fractional decrease of the outer lines of the triplet in molten TNT as a function of temperature.

kinetics of the decay is not first order. The center line of the triplet shows evidence of decay above 220 °C.

When unirradiated TNT is heated at 210 °C for 4 hours a triplet spectrum is also formed in which each line has equal intensity and equal separation of 8 *G*. This spectrum appears to be the same as the high temperature triplet obtained by uv irradiation at room temperature and recorded at 175 °C. With continued heating at 210 °C the outer lines of this triplet decay and one resonance remains at the center. What appears to be occurring is the loss of the 1 : 1 : 1 triplet and an increase of a singlet species.

When uv irradiated 2,4,6 TNT was dissolved in benzene and the spectrum recorded at room temperature a dominant three line spectrum with line separations the same as that observed in molten TNT was observed. However, unlike the molten TNT further hyperfine structure was evident on each of the three lines, indicative of hyperfine interaction with a number of hydrogen atoms. Although all of the lines were not resolved those that were had a separation from the adjacent lines of 2.5 *G*. The highest and lowest field lines of the spectrum which were resolved could be accounted for by assuming an equal interaction

TABLE I

Spin Hamiltonian parameters of nitroso radicals in nitrotoluenes obtained from frozen benzene solutions of the irradiated material

	Hydrogen	A_n	Nitrogen				
	A_h	(Gauss)	$A_\parallel$	$A_\perp$	$g_\parallel$	$g_\perp$	Radical
4,6 DNT	2.5	10.0	25.0	2.5	2.002	2.006	$C_6H_3(CH_3)(NO_2)NO^-$
2,4,6 TNT	2.5	10.0	25.5	2.25	2.003	2.007	$C_6H_2(CH_3)(NO_2)_2NO^-$
3,4,5 TNT	2.5	10.0	24.0	3.0	2.002	2.006	$C_6H_2(CH_3)(NO_2)_2NO^-$

of 2.5 *G*. with five hydrogen nuclei. The powder spectrum recorded when the benzene was frozen yielded the same nitrogen hyperfine tensor components as those obtained from the spectrum in the irradiated powders.

Spectra having the same isotropic nitrogen splitting, hyperfine tensor components, and *g* tensor components were observed when uv irradi-

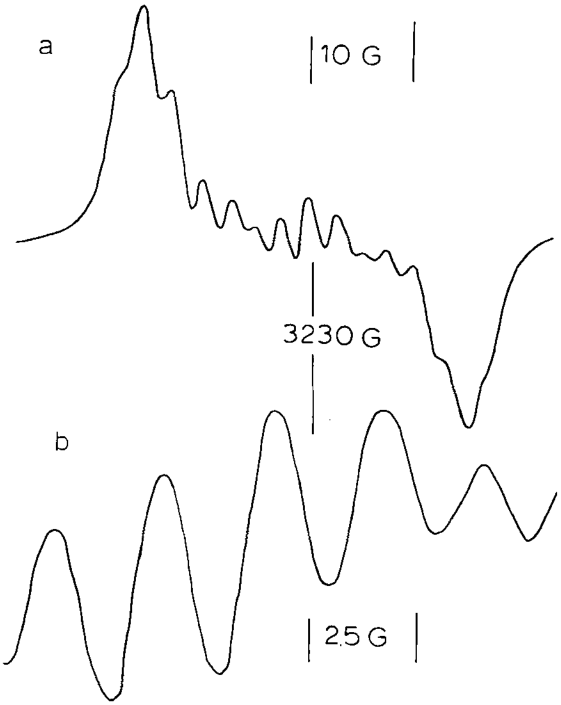

FIGURE 5 (a) EPR spectrum of irradiated DNT dissolved in benzene. (b) Spectrum on an expanded scale showing detailed hyperfine splitting at center.

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ated 3,4,5 TNT and 3,5 dinitrotoluene were dissolved in benzene and the spectra recorded below the freezing point of benzene. In the liquid state the H hyperfine interaction was partially resolved. The spin Hamiltonian parameters for the nitrotoluenes in benzene are given in Table I. All of the resolved hydrogen hyperfine lines in DNT were separated from their adjacent lines by 2.5 *G*. The magnetic field position of the highest and lowest field resonances of the spectrum was consistent with an equal interaction with 6 hydrogen nuclei. Figure 5 shows the spectrum of DNT dissolved in benzene, at 30 °C.

DISCUSSION

The EPR spectrum in the decomposed TNT is due to an unpaired electron having a Fermi hyperfine interaction of 12 *G*. with a nitrogen nucleus and principle components of the nitrogen hyperfine interaction of $A_{\parallel} = 27.0$ and $A_{\perp} = 4.0$ *G*. Because of the further hyperfine interaction with the five hydrogen nuclei it is clear the radical is associated with the TNT molecule. The fact that spectra having the same nitrogen hyperfine tensor components, and *g* tensor components could be obtained in 3,4,5 TNT and 3,5 DNT indicates the unpaired electron density of the radical is independent of the position and the number of NO_2 groups on the molecule. This would suggest that most of the unpaired electron density is not localized on the ring but rather is concentrated on a group attached to the ring. This would argue against, for example, an anion of TNT, where localization of unpaired density is on the ring and in which differences in splitting with the different nitro nitrogens would be expected. The EPR of the anion of TNT has been observed, and indeed the hyperfine interactions with the different nitrogens depend on the nitrogens position on the ring.[4]

The nitrogen isotropic splitting and the principle components of the nitrogen hyperfine tensor are consistent with localization of the unpaired electron density on the NO group.[5,6] For example the nitrogen hyperfine tensor components of di-t-butyl nitroxide are $A_{\perp} = 6.3$ and $A_{\parallel} = 32.0$ *G*.[6] However, even more suggestive, are EPR studies of the stable nitrosobenzene anion, $C_6H_5NO^-$, which give an isotropic splitting with the nitrogen nucleus of 11.3 *G* quite close to that measured here. Also in this radical the hydrogen interaction with the ortho and para hydrogens was 2.4 *G*. similar to the measurement here. Based on these considerations the radical observed in TNT is assigned to the nitroso anion of TNT, $(CH_3)C_6H_2(NO_2)_2(NO)^-$. The equivalency of the hyperfine interaction of the three methyl hydrogen nuclei and the

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two ring hydrogens is probably fortuitous and some differences may exist beyond the resolution of the spectrum. However, it is interesting that a similar equivalency of methyl and ring hydrogen splittings was observed in EPR studies of *N* nitroso *p* tolyl nitroxide and was 2.8 *G*.[8]

The radicals observed in 3,4,5 TNT and 3,5 DNT have almost identical nitrogen isotropic hyperfine splittings, nitrogen hyperfine tensor components and principle components of the *g* tensor. This would strongly suggest that these radicals are structurally similar to the radicals observed in 2,4,6 TNT. In liquid benzene the spectrum of 3,4,5 TNT and 3,5 DNT showed partially resolved hydrogen hyperfine interactions. In 3,4,5 TNT it was clear that this interaction was with 5 hydrogen nuclei. Similarly in 3,5 DNT the spectrum could be accounted for by interaction with 6 hydrogen nuclei. The highest and the lowest hydrogen hyperfine lines could be accounted for on the assumption of an equal interaction with 6 hydrogen nuclei. In 3,5 DNT an equal interaction with three ring hydrogens would be expected, no matter which NO_2 the NO was formed on, since there are no meta hydrogens with respect to the NO. Generally hyperfine interactions with ortho and para are equal but interactions with meta hydrogens are smaller. In 3,4,5 TNT the situation is a little more complicated. For the NO formed at position 5, there would be one ortho hydrogen and one para hydrogen. The situation would be the same for the NO formed at position 3. However for the NO formed at position 4 there would be two meta hydrogens. Assuming that the radical can be formed with equal probability from a 3, 4 or 5 nitro and since meta hydrogen interactions are usually smaller than ortho and para hydrogens, the spectrum would be expected to consist of an overlap of two spectrum one with an equivalent interaction with 5 hydrogen nuclei which would be twice as probable as the other spectrum with an inequivalent interaction to the hydrogen nuclei. Thus the dominant spectrum would be determined by an equal interaction with five hydrogen nuclei, and indeed the positions of the high and the low field hyperfine lines of the hydrogen interaction in 3,4,5 TNT are predicted of the basis of an equal interaction with five hydrogen nuclei.

The assignment of the radical to the nitroso derivative of TNT is consistent with previous studies of the decomposition of TNT using different techniques. X-ray photo electron spectroscopy (XPS) of uv and thermally decomposed TNT show that the peak due to the emission of electrons from the 1S level of the nitrogen at 407. eV decreases and a new peak at 401.0 eV grows. This new peak was conclusively shown to be associated with the nitroso derivative of TNT formed by the removal of the oxygen from the NO_2 group.[9]

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Other studies of the decomposition of TNT using mass spectrographic and time resolved optical techniques point to the formation of nitroso products of TNT.[10,11] EPR studies of the photolysis of 2,4,6 TNT in ether solvents have been reported and the radicals observed were believed to be a result of the interaction of an excited state of TNT and the solvent involving an abstraction of a H atom from the solvent.[12] The spectra observed here in the molten TNT do not appear to be the same as those produced in the ether solvent. Some previous studies of thermally decomposed TNT reported the formation of three radicals and measured their kinetics of decay.[2] Initially a complex spectrum was produced at 220 °C consisting of twenty lines. This decayed after an hour at 220 °C. Also observed was a simultaneous growth of a broad singlet with two satellite resonances on either side. The separation of the two satellite resonances from each other was the same as the separation of the outer two resonances of the triplet observed here. It is likely that these satellite lines are the same as the resonances observed here. No assignment of the spectrum was made in this work.

The irreversible decrease of the nitrogen isotropic hyperfine interaction with increasing temperature is suggestive of a further chemical change or a conformational change in the radical. The frequency of exchange between the two forms can be related to the decrease in the hyperfine splitting with temperature by,[13]

$$\nu = \frac{2}{\sqrt{2}}\gamma_e\left(A_0^2 - A^2\right)^{1/2} \tag{2}$$

where A_0 is the splitting in the absence of exchange and γ_e is the gyromagnetic ratio. For a thermally activated process the temperature dependence of the exchange frequency will be given by,

$$\nu = \nu_0 \mathrm{EXP}(-E/kT) \tag{3}$$

where E is the activation energy for the process. Figure 6 shows that the log of the exchange frequency plotted against the reciprocal of the absolute temperature is a straight line. An activation energy of 0.45 ± .05 eV is obtained from the data.

At temperatures above 185 °C, the outer lines of the triplet anneal and a new single resonance appears to grow at the center. The kinetics of the decay of the outer lines is clearly not a first order process as indicated on the semi-log plot of Figure 4.

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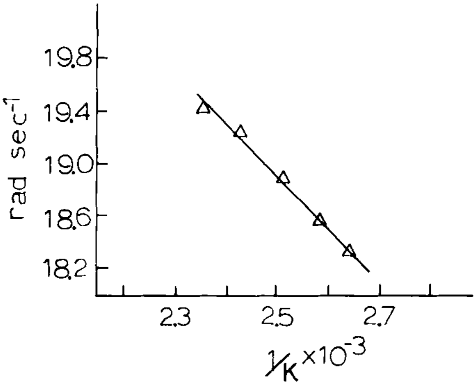

FIGURE 6 Plot of the log of the calculated exchange frequency deduced from the temperature dependence of the hyperfine splitting in the molten phase of TNT versus the reciprocal of the absolute temperature.

Since heat can initiate explosion and as demonstrated here and in previous work, can produce radicals, the results provide some support for the role of radicals in the initiation of explosion. The question of whether the radicals observed here play an important role in the process is more difficult. The only observation that can be made is that the temperatures at which the radicals can be produced are temperatures which can induce explosion.

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