

studies were useful in the sense that they ensured that equilibration of CO between the solution and the gas phase was not a limiting factor (since the rate of substitution was so much faster than that for the other compounds). In reactions at $-30\text{ }^{\circ}\text{C}$ with only moderate stirring, plots of $\ln A$ vs. time were linear through only 1 half-life, and the rates corresponded to $t_{1/2}$ about 4 min. With more vigorous stirring, such that the reaction vessel shook from the vibration of the stirrer, the plots were linear through 4 half-lives and a $t_{1/2}$ of 45 ± 10 s was obtained in four separate experiments. We therefore consider the half-life of 45 s to be an upper limit, and the actual value may be lower. A more detailed investigation of this reaction is in progress.

Reaction of $\text{Co}_2(\text{CO})_8$ with ^{13}C in the Presence of $\text{HCo}(\text{CO})_4$. The rate of substitution of $\text{Co}_2(\text{CO})_8$ with ^{13}C at $0\text{ }^{\circ}\text{C}$ in heptane was measured and as shown in Table I agrees with the previously reported values. In a second experiment, $\text{HCo}(^{13}\text{C})_4$ (with 86% substitution) was prepared and 5 mol % added shortly after initiation of the reaction. The rates of reaction were identical within experimental error to those in the absence of added $\text{HCo}(\text{CO})_4$.

In a third experiment, $\text{Co}_2(^{13}\text{C})_8$ substituted to Presence extent of 86% was prepared. The rate of substitution of ^{12}C was studied in these reactions in the presence of 330 mol % of $\text{HCo}(^{12}\text{C})_4$. The rate of incorporation of ^{12}C was slightly slower in these reactions but not outside the limits of experimental error.

Reaction of 1 with $\text{HCo}(\text{CO})_4$. All reactions were run in thermostated vessels at $25\text{ }^{\circ}\text{C}$ and normally 1 atm of CO. The reactions run at higher pressures were measured by using a mechanical gauge, accurate within 10% as calibrated against a mercury manometer. The reactions were initiated by injecting a solution of the hydride to the vigorously stirred solution of the alkyl. The course of the reaction was followed by the infrared spectrum, following the production of $\text{Co}_2(\text{CO})_8$ and EtOAc, and the decrease in concentration of 1 using the extinction coefficients quoted below. The concentration of the hydride solutions was determined by alkaline titration and the concentration of the alkyl solutions by cobalt analysis. Ethyl acetate was also measured at the end of the reactions using GC. The stoichiometry in every case corresponded to that shown in eq 1, and there was no sign of carbonylated products in either the IR or the GC. Initial rates were determined from the first 0-15% of reaction. Solutions of 1 stored for 10 days at room temperature under CO in the presence of a 10-fold excess of $\text{Co}_2(\text{CO})_8$ showed no signs of

decomposition, as detected by IR spectroscopy.

Reduction of 1 with H_2 . One milliliter of a 0.057 M solution of 1 in *n*-heptane was placed in a 5-mL glass rocking autoclave and pressurized to 25 bar with H_2 . The color of the solution gradually turned brown. After 40 min of agitation at $32\text{ }^{\circ}\text{C}$, the IR spectrum of the reaction mixture showed 69% conversion to $\text{Co}_2(\text{CO})_8$ and ethyl acetate in a 1:2 molar ratio.

Kinetic runs were performed in a gasometric apparatus fitted with a mercury-filled gas burette. A 5-L buffer flask was connected to the leveling vessel of the gas burette and kept at the pressure of the reaction vessel. All parts of the apparatus were thermostated ($\pm 0.05\text{ }^{\circ}\text{C}$). The actual total pressure was determined in mmHg by using an open mercury manometer measuring the pressure difference between the atmosphere and the reaction vessel. The change of IR spectra was followed from samples taken with a syringe and measuring in a CaF_2 IR cell: Absorptions 1857 cm^{-1} , $\epsilon_M(\text{Co}_2(\text{CO})_8)$ $1735\text{ cm}^2\text{ mmol}^{-1}$,²² 1745 cm^{-1} , $\epsilon_M(\text{EtO-COCH}_3)$ 743; 1715, $\epsilon_M(1)$ 820. Initial rates were calculated from graphical plots below 5% conversions.

Reaction of 1 with Ph_3P . These reactions were performed in the gasometric apparatus described above and started by injecting 1 in *n*-heptane into solutions containing known amounts of Ph_3P in *n*-heptane. Pale yellow crystalline $\text{EtOOCCH}_2\text{Co}(\text{CO})_3(\text{PPh}_3)$ could be isolated with 80% yield from the reaction mixtures after 92% of the calculated amount of CO was given off in 48 h at $25\text{ }^{\circ}\text{C}$. Initial rates were calculated from graphical plots below 5% conversions.

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Theoretical Studies of Radical Recombination Reactions.

1. Allyl and Azaallyl Radicals

J. J. Dannenberg* and K. Tanaka

Contribution from the Department of Chemistry, City University of New York—Hunter College and The Graduate School, New York, New York 10021. Received August 23, 1984

Abstract: The reaction paths for the recombination of methyl radicals with allyl, 1-azaallyl (both for attack on C and N), and 2-azaallyl radicals have been studied by using the MNDO approximation to molecular orbital theory with 3×3 CI and complete geometrical optimization. The methyl/allyl and methyl/2-azaallyl recombinations are predicted to have activation enthalpies of 5.5 and 5.6 kcal/mol, respectively, while the methyl/1-azaallyl recombination is predicted to have activation enthalpies of 3.9 and 11.0 kcal/mol for attack on C and N, respectively.

The recombination of two free radicals to form a stable covalent bond (or bond homolysis, the reverse reaction) is a process that is fundamental to the study of chemical reactivity. As such, it is discussed in virtually all textbooks on organic chemistry. The process is generally thought to occur without any activation energy (presumably, this is what would be expected by analogy to the recombination of two hydrogen atoms) except in cases, such as the recombination of two Ph_3C radicals, where steric hindrance may be involved. Despite the lack of direct evidence for it, and a growing body of evidence that suggests that there may be causes of activation for recombination of two radicals other than steric hindrance, this idea persists.

In fact, activation energies have long been reported for recombination of alkyl radicals (for example, ethyl¹) and for chain termination of various radical polymerization reactions.² Similarly, differences in the rates of radical recombination reactions that might be expected to have the same Arrhenius preexponential factors have been reported. Thus, two methyl radicals recombine 6 times as fast as two trifluoromethyl radicals.³

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Salem has shown that for certain photochemically induced bond cleavages, such as α cleavage in ketones, the π, π^* state of the ketone correlates with the ground state of the radical pair, while the n, π^* state of the ketone correlates with an excited state of the radical pair⁴ (the ground state of the ketone also correlates with the ground state of the radical pair in this case). The problem of surface crossings in photochemical and chemiluminescence reactions has been examined by Salem, Turro, Dauben, Evleth, and others.⁵ Their treatments imply (although they do not explicitly address this point) that there may be cases where surface crossings are necessary for radical recombination reactions. If such cases can be identified, they may lead to the prediction and observation of activation energies for certain radical recombination reactions.

Another related recent area of research has been the study of "orbital isomerism" in free radicals, chiefly the differences in the properties of σ and π radicals.⁶ The succinimidoyl radical has been prominent in these studies, although Skell^{6a} and Dewar^{6b} have suggested other radicals where similar behavior to that observed for succinimidoyl might be anticipated.

In our own work,⁷ we have predicted barriers to the recombination of $\text{CH}_3\text{CH}_2\text{NN}\cdot$ with $\text{CH}_3\text{CH}_2\cdot$ to form any of the three isomeric 1,1- and 1,2-diazenes. A significant contributing factor to this barrier may be related to the problem of orbital isomerism in the $\text{CH}_3\text{CH}_2\text{NN}\cdot$ radical

In principle, even the recombination of two halogen atoms could have an activation energy as eight of the nine possible ways of combining two chlorine atoms lead to repulsive excited states.⁸ If the initial long-distance attraction between two approaching halogens were most favorable in an excited-state symmetry, there could be a barrier to recombination. This situation could arise if interactions other than covalent bonding be strongest at long interatomic separations.

In a recent article, Sanderson evaluates "radical reorganization energies", which constitute the difference between the observed bond dissociation energy for a particular bond and the "contributing bond energy" (which is the intrinsic energy of the type of bond being broken, irrespective of substituents).⁹ The radical reorganization takes place during bond breaking. The reverse reorganization expected during radical recombination could lead to activation energies if they be great enough and take place at a favorable part of the reaction path.

In principle, one might expect some kind of activation energy for the recombination of free radicals when one or more of the following processes are involved in the recombination reaction: (a) geometrical reorganization, (b) electronic reorganization (including problems involving state correlations), and (c) the predominant interaction between the radicals at large separations differing from that at short separations. The contributions of one or more of these phenomena to an activation energy should become more observable for recombination reactions that are less, rather than more, exothermic. Some cases where recombination to a covalent product is only weakly exothermic will also receive some attention.

The purpose of the work described in this paper is to begin to determine which, if any, of these effects exist, to identify the chemical situations where they would be expected, and to estimate their magnitudes or relative magnitudes. In this study we have calculated the reaction paths for the recombination of methyl radical with allyl radical to form 1-butene, with 2-azaallyl radical

Table I. Energetics of Combination Reactions (kcal/mol)

	allyl	2-azaallyl	1-azaallyl, attack on C	1-azaallyl, attack on N
ΔH_f of radical	35.3	42.9	42.0	42.0
ΔH_f of col	66.6	74.3	71.7	78.8
ΔE_{act}	5.5	5.6	3.9	11.0
ΔH_f of product	0.3	10.2	4.3	15.1
ΔH of reaction	-60.7	-58.4	-63.4	-52.6

Table II. Significant Features of the Transition States for Recombination Reactions

	allyl	2-azaallyl	1-azaallyl, attack on C	1-azaallyl, attack on N
dist (CH_3 -radical), \AA	2.50	2.50	2.70	2.30
angle CH_3 -allyl (1-2), deg	104.4	104.4	103.0	112.0
dihedral CH_3 -allyl (1-2-3), deg	92.0	92.0	94.2	106.6
dist (allyl 1-2), \AA				
radical	1.383	1.329	1.436	1.298
col	1.401	1.350	1.442	1.316
difference	-0.017	-0.020	-0.005	-0.017
dist (allyl 2-3), \AA				
radical	1.383	1.329	1.298	1.436
col	1.372	1.315	1.297	1.415
difference	0.011	0.014	0.001	0.021

Table III. Heats of Formation (kcal/mol) as a Function of Bond Distance

separation, \AA	ΔH_f , H-H	ΔH_f , CH_3 -H	ΔH_f , CH_3 - CH_3
0.67	-0.3		
0.80	4.9		
1.00	25.4		
1.09		-12.3	
1.50	79.3	21.4	
1.52			-18.6
1.80	95.3		0.1
2.00	100.1	66.3	22.3
2.20	102.5		39.9
2.50	103.8	77.3	52.3
2.70			54.0
3.00	104.2	78.1	53.6
3.50		78.0	52.3
4.00	104.2	77.9	
∞	104.2	77.9	51.6

to form 2-aza-1-butene, and with 1-azaallyl radical to form both methylvinylamine and 1-aza-1-butene. The allylic species are chosen to illustrate the effects of electronic and skeletal rearrangements on the activation energy for radical recombination.

Methods

All calculations were performed by using the MNDO approximation to molecular orbital theory¹⁰ with 3×3 configuration interaction (CI). The configurations used were the two that localize the highest energy pair of electrons in the HOMO of each radical and the one that places one electron on each radical. The reaction paths were studied in the reverse (bond cleavage) direction. The geometries were optimized in all variables for each fixed value of the reaction coordinate (29 for allyl or 26 for azaallyl plus methyl) without any other constraints. Final optimizations were performed by using 3×3 CI, as indicated.

Results

The calculated heats of formation and enthalpies of activation of the various species involved in the recombination of $\text{CH}_3\cdot$ with allylic radicals are collected in Table I, while the most important structural features of the relevant species are indicated in Table II. As is often the case, the potential surface was found to be rather flat in the direction of the reaction coordinate at the col. The energy varied by only 0.1–0.2 kcal/mol with a change of 0.1 \AA in reaction coordinate.

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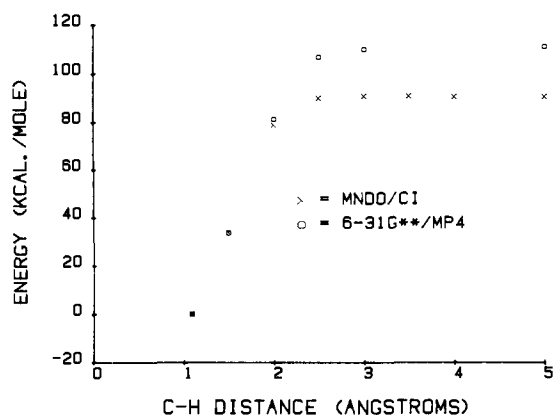
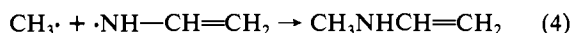
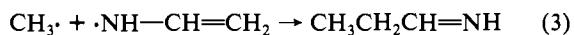
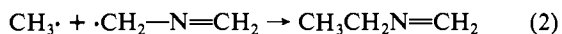
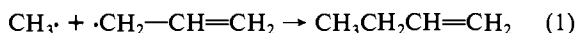


Figure 1. Comparison of MNDO/CI and ab initio dissociation curves for methane.

The dissociations of H-H, CH₃-CH₃, and CH₃-H are collected in Table III. The MNDO/CI reaction path for the last reaction is compared with UHF/6-31G** reaction paths with and without correction for electron correlation, as reported by Schlegel et al.,¹² in Figure 1.

Discussion

The activation energies and cols for the recombination of methyl radical with the allyl and 2-azaallyl radicals (reactions 1 and 2)



are similar. As the singly occupied orbital of both radicals are virtually identical, the only differences must involve the filled orbitals, which do not significantly affect the interaction energy.

The activation energies for the two different reaction paths for recombination of methyl with 1-azaallyl radical differ significantly from each other. Attack on carbon (reaction 3) is clearly favored over attack on nitrogen (reaction 4). All of the recombination reactions studied are extremely exothermic. As such, one would expect the transition states to resemble the radicals by virtue of the Hammond postulate,¹¹ which they do to a large extent. Figure 2 illustrates the differences in the structures of the transition states for the most and least favored reactions (eq 3 and 4, respectively). Clearly, in reaction 3, which is the most exothermic and has the lowest activation energy, the transition state most resembles the radicals. In particular, the C=N double bond is already significantly localized in the azaallyl radical, leaving the unpaired electron more localized on the terminal carbon. The methyl radical attack is more from beneath the azaallyl radical than for attack at nitrogen where the attack is at a more obtuse angle which reflects the structure of the product whose nitrogen lone pair will be conjugated with the π -bond (see Figure 2). The greater electronegativity of nitrogen causes it to fill its valence shell at the expense of carbon, thereby leaving more of the unpaired spin density on the carbon end of the radical. For attack at carbon, the higher density of the unpaired electron on the carbon causes increased overlap of the half-filled orbital with that of the approaching methyl radical, which is manifest in greater bonding at longer distances. Attack at the nitrogen end is disfavored because there is relatively less unpaired electron density there. To develop density on the nitrogen, nuclear movement must accompany polarization of the electrons, resulting in a lengthening of the C-N bond and a shortening of the C-C bond in the allylic fragment. To the extent that this behavior leads to an activation energy, one should expect recombinations involving other delocalized radicals to also have activation energies.

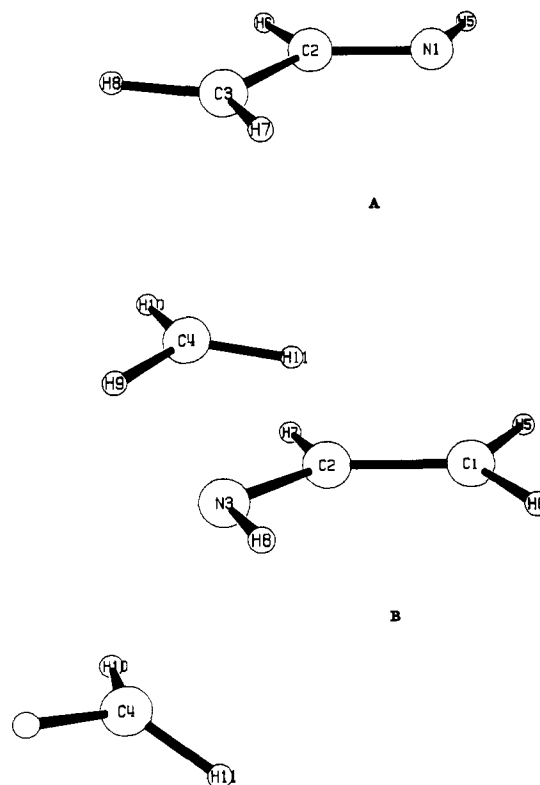


Figure 2. ORTEP drawings for the transition states of reactions 3 (A) and 4 (B).

Another cause of the higher activation for attack at nitrogen is that nitrogen has lower energy and more compact atomic orbitals available for the new σ -bond than does carbon. Consequently, the methyl radical must approach more closely to nitrogen than carbon to obtain an equivalent overlap. Since the nitrogen orbital will be lower in energy than that of carbon, the bonding interaction for a given overlap will be less than for attack at carbon where two orbitals of equivalent energy interact. In order to form a better bond to nitrogen, the methyl radical might tend to pyramidalize in order to increase the s character and, thereby, increase the electronegativity of the half-filled methyl orbital. As the s character is increased, the density at long distance from the carbon nucleus will be decreased, thereby further decreasing the overlap between carbon and nitrogen. To the extent that this effect is important, radical attack might be expected at the larger, more polarizable site of a multidentate radical.

To a reasonable extent, it appears that the relative activation barriers to the reactions studied might have been predicted by using frontier orbital theory. There are two significant differences from the normal application of frontier orbital theory, however. First, there are no HOMO's and LUMO's, as such, to undergo the kind of bonding interactions that are reasonably treated by the usual perturbation theory arguments; rather there is a direct bonding interaction between two unpaired electrons. Second, the perturbation theory arguments associated with frontier orbital theory are essentially indicative of the slope of the energy of the reactants with respect to movement along the direction described by the perturbation. Since radical recombinations may often have no activation, the slopes in one or more directions may be negative, in which case they would be of no predictive value.

An important consideration must be the level of confidence one can expect from calculations of the type described here. There are not other studies using fully optimized MNDO/CI calculations to estimate the barriers for radical recombinations of which we are aware except for our own work on the thermal decomposition of azoalkanes and 1,1-dialkyldiazenes⁷ and the cases mentioned below. Large basis set ab initio calculations with complete optimization at the UHF SCF limit with correction for electron correlation are not feasible for reaction paths involving so many basis functions and geometrical degrees of freedom. Comparison

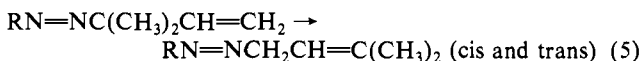
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can only be made for less complex reaction paths where little or no barrier is expected.

The dissociation reaction paths for H-H and CH₃-H are both uneventful in that no barrier is found for the reverse reaction. In addition, the reaction coordinate diagram for the latter reaction is remarkably similar to that calculated by Schlegel¹² using an UHF/6-31G** ab initio technique. The dissociation energy is lower than the experimental value due to a relatively large error in the calculated heat of formation of CH₃· combined with an error in the MNDO/CI heat of formation for methane. These errors are larger than normally encountered with MNDO. Our results on CH₃-H agree, qualitatively, with those of Engelke,¹³ who found no barrier to recombination using MNDO with 2 × 2 CI. The 2 × 2 CI procedure starts with a closed- (rather than open-) shell ground-state function which does not converge to the sum of the radical energies at long C-H separations. The 3 × 3 CI procedure starts with the expected singlet open-shell wave function (using the half-electron method)¹⁰ which is consistent with the calculation of the individual radicals. Clearly there are no major qualitative artifacts caused by the MNDO/CI method on these dissociation reactions, although there are some quantitative errors. Qualitative artifacts have been found for dissociation/recombination reactions involving radical sites at oxygen and fluorine,¹⁴ but these are special cases that will be discussed elsewhere together with the effects of extended CI.¹⁴

As always, we suggest that experimentation should be the test of the proposed reaction paths. Recent experimental reports^{15,16} have supported the mechanism for the thermal decomposition of diazenes suggested by MNDO/CI calculations.⁷ In particular, recombination of alkyl and alkyldiazenyl radicals has been observed to compete with the decomposition of alkyldiazenyl radicals to form nitrogen gas and alkyl radicals.^{15,16} Another aspect of the proposed mechanism is the suggestion of an activation energy for the recombination of the alkyl/alkyldiazenyl radical pair to reform azoalkane.

Engel¹⁶ has recently reported the formation of "turnaround" (TA) azoalkane during the decomposition of cis unsymmetrical azoalkanes where one of the alkyl groups is 3,3-dimethyl-3-propenyl (reaction 5). Although Engel assumes no activation

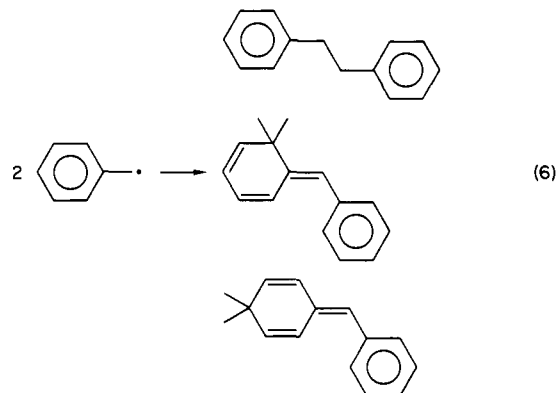


energy for this process, his results are not in disagreement with a small activation. To the extent that the TA azoalkane is formed from the caged radical pair, recombination is competitive with decomposition of the alkyl diazenyl radical. However, to the extent that alkyldiazenyl radicals can escape from the solvent cage, diffusion out of the cage must be competitive with recombination.

The bimolecular rate for diffusion-controlled reactions in normal solvents at 25 °C is generally assumed to be in the range 10⁹ to 10¹⁰ M⁻¹ s⁻¹. Assuming an *A* factor of 10¹³ (which should be

corrected by the statistical factor of 1/4 to reflect the necessity of paired spins in the product) for radical recombinations, one can calculate Arrhenius *E*_{act} of 4 to 6 kcal/mol for reactions that would take place at this rate if not retarded by diffusion. Reactions with *E*_{act}'s lower than this value will appear to be diffusion controlled. It follows that a similar rate must apply to diffusion of two radicals away from each other. Reactions with activations below a similar threshold calculated by using the Arrhenius equation should occur faster than diffusion from the cage. To the extent that diazenyl radicals diffuse out of the cage, they favorably compete with recombination, which must, then, have an activation energy. Although Engel presents no evidence on this point, there is reason to believe that at least the phenyldiazenyl radical must live long enough to diffuse out of the cage.

Fischer¹⁷ and McBride¹⁸ have reported recombination of benzyl and α-methylated benzyl radicals, respectively, to give a mixture of bibenzyls and semibenzenes (reaction 6). Fischer¹⁷ reports



that 19% semibenzenes are among the primary products of the recombination of benzyl radicals at 30 °C. The recombination of these radicals has been reported to be diffusion controlled.¹⁷ Fischer's suggestion that different complexes of benzyl radical pairs that lead to different products may exist is consistent with an activation energy for the collapse of these complexes to form product, as they could not be true minima on a potential surface if there were no barrier to recombination to form product.

Finally, it has long been established that 1-azabutadiene and its derivatives do not readily undergo Diels-Alder reactions as dienes.¹⁹ This behavior might be explained by analogy to the reaction paths that we have calculated for the recombination of the methyl and 1-azaallyl radicals, to the extent that the transition state for such reactions has some diradical character.

Acknowledgment. This work was supported, in part, by a City University PSC-BHE grant.

Registry No. ·CH₃, 2229-07-4; ·CH₂CH=CH₂, 1981-80-2; ·CH₂N=CH₂, 56391-78-7; ·NHCH=CH₂, 50614-03-4; CH₃CH₂CH=CH₂, 106-98-9; CH₃CH₂N=CH₂, 43729-97-1; CH₃CH₂CH=NH, 4753-69-9; CH₃NHCH=CH₂, 2308-42-1.

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