J. Phys. Chem. A **1999,** *103,* 3904−3909

A New Mechanism for the Reaction of Carbenes with OH Groups

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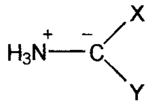
Received: September 28, 1998; In Final Form: February 8, 1999

The reaction pathway for the $2H_2O + CCl_2$ reaction through a cyclic five-atom transition structure was studied using ab initio molecular orbital theory. The MP2 method in conjunction with the DZP basis set was used for geometry optimizations, and single point energy calculations were performed at MP2 and MP4 levels with the cc-pVDZ and cc-pVTZ basis sets. The solvent effect on the activation free energy was evaluated by Monte Carlo statistical mechanics calculations. The new mechanism has a high rate constant, and we predict a lifetime of seven nanoseconds for dichlorocarbene in aqueous solution. We have proposed that this mechanism occurs for the reaction of dichlorocarbene with water, and possibly may be involved in many reactions of carbenes with alcohols. We have also shown that it can explain the following experimental facts: (a) alteration of the product isotopic effect on addition of a second alcohol, (b) difference between product and kinetic isotopic effects, and (c) no linear dependence of the observed rate constant for carbene decay on alcohol concentration.

I. Introduction

The electronic structure of carbenes allows them to act as electrophilic or nucleophilic species. The substituting groups bonded to the carbene center have a significant influence on these characteristics, and control its reactivity.[1] Thus, carbenes have a broad range of proton affinity,[2] and their reactions with atoms having lone pairs of electrons can present different behaviors. For example, methylene forms an ylide with water,[3] while dichlorocarbene does not.[4,5] In the last case, the chlorine atoms decrease the carbene electrophilicity. In the reaction with ammonia and amines probably all carbenes form ylides, due to a greater basicity of the nitrogen. In these examples, ylides are clearly dipolar species, with charge transfer from the heteroatom to the carbene, as illustrated below:



When dichlorocarbene interacts with C═O groups, a dipolar species is not formed. The carbon−oxygen π bond breaks down, and the formation of an ylide with biradical characteristics takes place.[6] The carbonyl ylides of methylene, difluorocarbene, and dihydroxycarbene with formaldehyde also exhibit biradical characteristics.[7−9] In the reaction of dichlorocarbene with C═N groups, dipolar and biradical species can be formed, although the biradical form is thermodynamically and kinetically more stable.[10] Based on these studies, the electrophilic properties of carbenes should be looked at with caution, since in general these species prefer to form biradical structures rather than dipolar ones. Furthermore, direct 1,2 cycloaddition of carbenes to the C═O bond is highly competitive with ylide formation.[6] These facts could explain why in some situations, as in reactions of arylchlorocarbenes with esters, the detection of the respective ylide failed to be accomplished, while the same carbene forms an ylide with acetone.[11] Only the most reactive arylchlorocarbenes were observed to form ylides with esters,[12] or when an aromatic structure can result.[13]

The above considerations lead us to inquire about the role of dipolar ylides in reactions of carbenes with OH groups. It seems to us that ylide formation should be an exception, instead of a rule. The observation of the isotopic effect in several reactions of carbenes with alcohols is another point unfavorable to the ylide mechanism.[14−17] A proton transfer mechanism seems probable only for the most basic carbenes, such as diarylcarbenes and possibly fluorenylidene.[2,18−20] Another proposed mechanism is the direct insertion via a three-center transition state. Recent experimental results have led to the suggestion of this mechanism when an isotopic effect is observed,[14,15] with the measured second-order rate constant being very high, in some cases about 10^9 L mol^{-1} s^{-1}. However, we have recently performed a high-level ab initio study coupled with Monte Carlo statistical mechanics simulation of the $H_2O + CCl_2$ reaction in the gas phase and in aqueous solution,[21] in order to determine the kinetics of this process by the insertion mechanism. We have obtained a rate constant of 2.8×10^{-4} L mol^{-1} s^{-1} in the gas phase, and 3.4×10^{-6} L mol^{-1} s^{-1} in aqueous solution. These values are very low, and we think that this reaction must occur through a mechanism different from the three traditional ones, i.e., proton transfer, ylide formation, and direct insertion. Therefore, in this work we have investigated an alternative mechanism, involving two water molecules in a cyclic transition state. As we will see, this mechanism leads to a high rate constant, and it is able to explain a series of intriguing facts concerning the reaction mechanism of carbene addition to alcohols.

II. Details of Calculations

Ab Initio Calculations. The search for minimum energy and transition state structures was performed at the ab initio MP2 level of theory using the Dunning's DZP basis set.[22] This was

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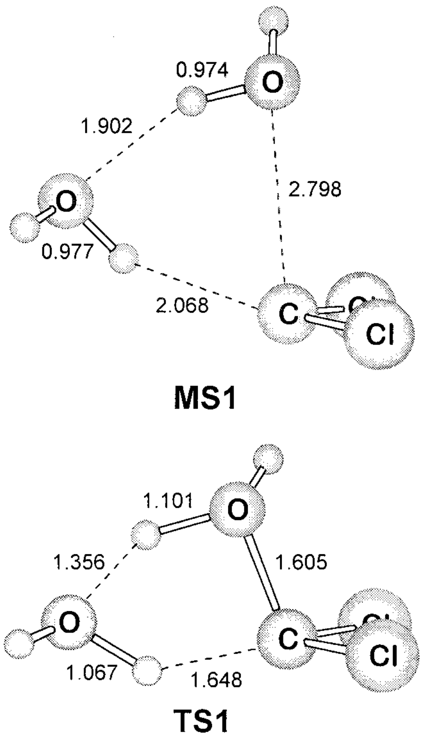


Figure 1. Minimum energy (MS1) and transition state (TS1) structures located on the potential energy surface for the $2H_2O + CCl_2$ reaction at the MP2/DZP level of theory.

TABLE 1: Relative Energies of the Stationary Points for the $2H_2O + CCl_2$ Reaction[a]

level/process	$2H_2O + CCl_2 \rightarrow MS1$	$MS1 \rightarrow TS1$
	DZP	
MP2	−14.96	3.34
ΔZPE[b]	4.21	−0.53
	cc-pVDZ	
MP2	−16.24	−0.98
MP4(SDQ)	−14.32	5.52
MP4	−15.25	3.54
	cc-pVTZ	
MP2	−14.52	0.95
MP4[c]	−13.54	5.47

[a] The geometries and harmonic frequencies were obtained at the MP2/DZP level. Units in kcal/mol. [b] Variation of zero point vibrational energy. [c] Obtained by additivity approximation.

based on a previous study of how H_2O interacts with CCl_2; thus we have emphasized the interaction of water with the sp^2 carbon.[5] The structures obtained, corresponding to the weakly bound complex (MS1) and the transition state (TS1) for water addition, are shown in Figure 1. The connection between MS1 and the $H_2O + CHCl_2OH$ products through the transition state TS1 was realized by intrinsic reaction coordinate (IRC) calculations using the Gonzalez and Schlegel method.[23] Higher level ab initio calculations using the MP2/DZP optimized geometries were performed to obtain more accurate stabilization and activation energies. Single point calculations were performed at the MP2 and MP4 levels utilizing the Dunning's cc-pVDZ and cc-pVTZ basis sets.[24,25] To save computation time, additivity approximation of correlation energy[26−28] was used to obtain the MP4/cc-pVTZ energies. The results are in Table 1.

TABLE 2: Thermodynamics and Kinetics Properties in Gas Phase and in Aqueous Solution for the $2H_2O + CCl_2$ Process[a]

	$2H_2O + CCl_2 \rightarrow MS1$	$MS1 \rightarrow TS1$
	Gas-Phase Values	
ΔE^b	−9.33	4.94
$\Delta H°$	−10.15	2.87
$\Delta G°$	6.34	7.97
ΔH^*	−8.97	2.87
$-T\Delta S^*$	11.53	5.10
ΔG^*	2.56	7.97
K, k^c	2.7×10^{-2}	8.9×10^{6}
	Aqueous Solution Values	
$\Delta\Delta G_{\text{solvation}}$	2.17	−1.24
$\Delta G^*_{\text{solution}}$	4.73	6.73
K, k^b	6.8×10^{-4}	7.2×10^{7}

[a] The symbols ° and * correspond to the standard state of 1 atm of pressure and 1 mol/L of concentration (see text). $T = 298.15$ K. Units in kcal/mol. [b] Variation of classical energy added to zero point vibrational energy. [c] Equilibrium (K, in units of $mol^{-2}\ L^2$) and rate (k, in units of s^{-1}) constants. The equilibrium constants were multiplied by a factor of 2 due the existence of two stereoisomers for MS1.

Thermodynamics and kinetics properties were determined by statistical mechanics analysis of the ab initio data. The results are in Table 2. We have used the symbols ° and * to represent the standard state of 1 atm of pressure and 1 mol/L of concentration, respectively. H* and S* are defined by the expressions

$$S^* = -\frac{\partial G^*}{\partial T} \qquad H^* = G^* + TS^*$$

So, the following relations are satisfied:

$$G^* = G° + RT \ln(\tilde{R}T)$$

$$H^* = H° - RT \qquad \tilde{R} = 0.082\,05\ \mathrm{K}^{-1}$$

$$S^* = S° - R \ln(\tilde{R}T) - R$$

With these definitions, the rate constant and Arrhenius parameters can be determined by the following relations based on transition state theory, irrespective of the molecularity of the reaction:

$$k(T) = \frac{k_b T}{h} e^{-\Delta G^*/RT}$$

or

$$k(T) = A e^{-E_a/RT}$$

$$E_a = \Delta H^* + RT \qquad A = \frac{k_b T}{h} e^{(\Delta S^*/R)+1}$$

All ab initio calculations were performed using the GAUSSIAN 94 system.[29]

Intermolecular Potentials. The solute−solvent potential was described using the site−site model, with charge−charge plus 12-6 Lennard-Jones interaction terms, in accordance with the following expression:

$$U_{ab} = \sum_{ab} \frac{q_i q_j e^2}{{r_{ij}}^2} + \frac{4\epsilon_{ij}{\sigma_{ij}}^{12}}{{r_{ij}}^{12}} - \frac{4\epsilon_{ij}{\sigma_{ij}}^{6}}{{r_{ij}}^{6}}$$

where q_i, ϵ_{ii}, and σ_{ii} terms belong to site i of molecule a, and q_j, ϵ_{jj}, and σ_{jj} terms belong to site j of molecule b. The crossing terms were obtained by the combination rules:

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \qquad \sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}}$$

TABLE 3: Lennard-Jones Parameters Used in Monte Carlo Simulations

atom/ parameter	ϵ (kcal/mol)	σ (Å)
C	0.105	3.75
O	0.1521	3.15061
Cl	0.300	3.40

The charges were calculated by the CHELPG scheme, which is based on fitting point charges in order to reproduce the molecular electrostatic potential.[30] We have used the MP2/DZP wave function with dipole restriction to perform the CHELPG calculations. The ϵ and σ constants were taken from OPLS parameters.[31,32] The interaction sites were placed on the atoms with the exception of CCl_2, to which was added a fourth site in order to better represent the carbon lone pair.[21] The Lennard-Jones parameters are in Table 3.

Monte Carlo Simulations. Liquid simulation by the Monte Carlo method was performed in order to determine the solvent effect (aqueous solution) on the activation free energy for the $2H_2O + CCl_2$ reaction. The solvation free energy of minima and of the transition state was calculated by statistical perturbation theory using double-wide sampling.[33] The simulations were conducted at isothermal−isobaric ensemble (NPT) and consisted of 9×10^5 configurations for equilibration and 2×10^6 configurations for average. We have used a rectangular box with 216 TIP3P water molecules as solvent. Metropolis and preferential sampling were used, the solutes were moved each 50 configurations and the volume was varied for each 1250 configurations. The translations and rotations were adjusted to lead to ca. 40% of acceptation rate. A cutoff of 8.0 Å for solute−solvent and solvent−solvent interaction was used. The environmental conditions were fixed in 1 atm and 25 °C. In accordance with our previous report, the atomic charges on the water (as solute) were obtained by the CHELPG scheme, because the TIP3P water model presents higher charges, resulting in a nonuniform treatment of the solutes.

The coupling parameter $\Delta\lambda$ for perturbation calculations was set in 0.10, with exception of the annihilation of water, which needed smaller steps.[21] The sequence of perturbations and the respective free energy variations are in Table 4. In addition, this table presents the solvation free energy of each species obtained by combining the perturbation steps. The difference of solvation free energy can be added to the gas-phase free energy to obtain the solution free energy:

$$\Delta G^*_{\text{solution}} = \Delta G^*_{\text{gas phase}} + \Delta\Delta G_{\text{solvation}}$$

And the rate constant in solution will be given by

$$k(T) = \frac{k_{\text{b}}T}{h} \mathrm{e}^{-\Delta G^*_{\text{solution}}/RT}$$

These differences in free energy are in Table 2, which also presents the reaction rate constant in solution calculated by the above equation. The Monte Carlo simulations were performed using the BOSS program.[34]

TABLE 4: Results of Statistical Perturbation Theory Calculations by Monte Carlo Simulation (T = 298.15 K, 1 atm; units in kcal/mol)

perturbations	ΔG
H_2O (q = 0) → nothing	−2.583 ± 0.153
CCl_2 (q = 0) → H_2O (q = 0)	0.616 ± 0.145
TS1 (q = 0) → CCl_2 (q = 0)	−0.388 ± 0.134
MS1 ($\boldsymbol{q}$ = 0) → TS1 (q = 0)	−1.483 ± 0.053
H_2O → H_2O ($\boldsymbol{q}$ = 0)[a]	7.268 ± 0.147
CCl_2 → CCl_2 (q = 0)	1.395 ± 0.055
TS1 → TS1 (q = 0)	10.227 ± 0.228
MS1 → MS1 (q = 0)	10.463 ± 0.284

Solvation Process

species	$\Delta G_{\text{solvation}}$
H_2O[b]	−4.685
CCl_2	0.572
TS1	−7.872
MS1	−6.625

[a] For TIP3P water, this contribution is 8.575 ± 0.199 kcal/mol. [b] For TIP3P water, the solvation free energy is −5.992 kcal/mol.

III. Discussion

Dichlorocarbene forms a stable trimer with two water molecules. The interaction occurs through the carbon atom, with the formation of a hydrogen bond with the first water molecule and the interaction of the carbene vacant π orbital with the oxygen lone pair of the second water molecule. In addition, the water molecules form hydrogen bonds between themselves. This weakly bound complex, which is illustrated in Figure 1 (MS1), is the precursor of a transition state for the CCl_2 reaction with H_2O. The reaction occurs through the approach of the second water near to the carbon atom, followed by losing a proton to the first water molecule, which donates one proton to the carbene. The transition state that is shown in Figure 1 (TS1) illustrates the process. It can be noted that the O−C bond in TS1 (1.605 Å) is smaller than that in the MS1 complex (2.798 Å). In addition, it can be observed that the O−H bonds involved in the hydrogen bonds in MS1 are elongated. Therefore, we have a cyclic transition state structure, where the proper reactant (water) catalyzes its reaction with dichlorocarbene, forming $CHCl_2OH$ and liberating H_2O.

The stabilization energy of MS1 in relation to the free molecules and the activation energy through TS1 from MS1 are in Table 1. At the MP2/DZP level, MS1 is stable by 14.96 kcal/mol. The use of the cc-pVDZ basis set increases this energy to 16.24 kcal/mol. In addition, the use of a higher level of electron correlation (MP4) leads to a small decrease of the energy (15.25 kcal/mol). Our best level of theory, MP4/cc-pVTZ obtained by additivity approximation, predicts a stabilization energy of 13.54 kcal/mol. For the activation energy, the variation of the basis set and the level of electron correlation yield major effects. The activation energy at the MP2/DZP level is 3.34 kcal/mol. The use of the cc-pVDZ basis set decreases this barrier to −0.98 kcal/mol, i.e., there is no activation barrier at this level of theory. However, the more extended cc-pVTZ basis set predicts a barrier of 0.95 kcal/mol at the MP2 level. In addition, the MP4 level of electron correlation with this basis set increases the barrier to 5.47 kcal/mol. The final stabilization and activation energies including zero point vibrational contribution are 9.33 and 4.94 kcal/mol (see Table 2). Figure 2 presents the potential energy surface profile for this process.

The thermodynamical parameters given in Table 2 show that the formation of the MS1 complex has a small positive free energy (2.56 kcal/mol). Although it has a favorable enthalpy of −8.97 kcal/mol, the entropic term ($-T\Delta S^*$) has a positive value of 11.53 kcal/mol, resulting in a positive ΔG^*. In aqueous solution, the solvation has an unfavorable effect, increasing the free energy to 4.73 kcal/mol. This is due to the greater solvation of the free water in relation to the complex. The transition state presents a low activation enthalpy of 2.87 kcal/mol. However, the rigidity of the transition state in relation to the MS1 complex produces a positive entropic term ($-T\Delta S^*$) of 5.10 kcal/mol,

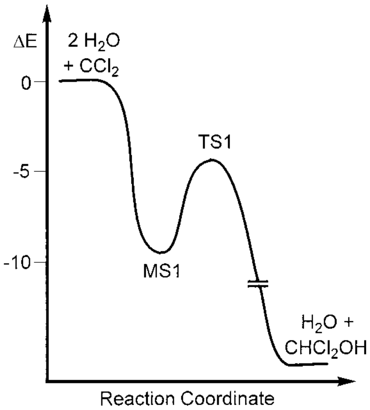


Figure 2. Potential energy surface profile for the $2H_2O + CCl_2$ reaction. Energies obtained at the MP4/cc-pVTZ//MP2/DZP level are added to the zero point vibrational energy calculated at the MP2/DZP level. Units of kcal/mol.

leading to an activation free energy of 7.97 kcal/mol. The aqueous solvent stabilizes the transition state in relation to MS1 by 1.24 kcal/mol, resulting in a final value of 6.73 kcal/mol for the activation $\Delta G^{*}_{\text{solution}}$.

Table 2 presents the equilibrium constant for MS1 formation and the rate constants for the MS1 → products reaction. We have used these data to calculate the pseudo-first-order decomposition rate of the CCl_2 in aqueous solution using the following equations:

$$2H_2O + CCl_2 \underset{}{\overset{K_{eq}}{\rightleftharpoons}} MS1$$

$$MS1 \xrightarrow{k_1} CHCl_2OH + H_2O$$

Because water is both solvent and reactant, the complex MS1 is included directly in the solvation of CCl_2. So, the formation of MS1 is just formal, and the expression for the reaction rate will be given by

$$\frac{d[CCl_2]}{dt} = -k_1 K_{eq} [H_2O]^2 [CCl_2]$$

Thus, the pseudo-first-order rate constant for decomposition of CCl_2 is given by

$$k_{obs} = k_1 K_{eq} [H_2O]^2$$

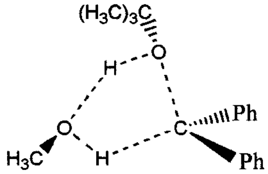
And

$$\frac{d[CCl_2]}{dt} = -k_{obs}[CCl_2] \qquad k_{obs} = 1.5 \times 10^8 \text{ s}^{-1}$$

On the basis of this mechanism, we predict that dichlorocarbene lives about 7 ns in aqueous solution. This lifetime is considerably smaller than our previous estimate of 1 h through a direct insertion mechanism.[21] This finding strongly supports the mechanism through a cyclic five-center transition structure (TS1) proposed in the present work, which we named the OH group catalysis mechanism.

Proposed General Mechanism for the Reaction of Carbenes with OH Groups. The OH group catalysis mechanism is considerably more favorable than the direct insertion for dichlorocarbene addition to water. This fact leads us to speculate that it can possibly be a very general mechanism, probably substituting for the direct insertion for various systems where it was proposed, i.e., in the reactions of carbenes with alcohols, for which the isotopic effect was observed. Naturally, each case must be investigated in order to give a definitive answer. Nevertheless, a careful look at this mechanism shows that it is very attractive, and it is able to explain several intriguing facts relative to reactions of carbenes with alcohols. Now, these points will be discussed.

Bethell and co-workers have investigated the reaction of diphenylcarbene with methanol and *tert*-butyl alcohol in acetonitrile solution and analyzed product isotopic effects.[35] They have observed that the isotopic effect on *tert*-butyl alcohol was affected by the presence of methanol. The product isotopic effect on *tert*-butyl alcohol was measured as $P_H/P_T = 5.4$ in the absence of methanol and 3.5 in the presence of methanol. They have proposed a reversible ylide formation mechanism to explain this effect. However, new experimental data do not support this picture.[18-20] Chateauneuf[19] has detected the formation of the diphenylcarbenium cation in experiments of laser flash photolisys of diphenyldiazomethane in acetonitrile−water solution as well as in methanol, ethanol, and propan-2-ol. These findings support the protonation mechanism for diphenylcarbene. Nevertheless, a more recenty study by Scaiano et al.[18] has indicated that just a minor part of the carbene generated in laser flash photolyses experiments is protonated. The major fate of diphenylcarbene is through a parallel pathway, which was proposed to be the direct insertion. The mechanism discovered in this work is also a possible alternative to the parallel pathway, and the observations relative to isotopic effects can be then accounted for. In accordance with the new mechanism, as two alcohol molecules are involved in the transition state, the addition of methanol changes the isotopic effect in the reaction of *tert*-butyl alcohol. This is because one molecule of methanol can participate in the transition structure, making a hydrogen bond with the carbene, while the oxygen lone pair of *tert*-butyl alcohol attacks the vacant π orbital of the carbene, as illustrated below: Thus, the OH group catalysis mechanism provides a single explanation for this effect, and we think that it should be considered as a real possibility for this case.



Another interesting experiment was performed by Zupancic et al.[36] They have studied the reaction of fluorenylidene with methanol in acetonitrile solution, and observed that the kinetic and product isotopic effect had different values. Again, a reversible ylide formation mechanism was proposed. In a very recent laser flash photolysis study of fluorenylidene by Olson and Platz,[37] they concluded that the ylide mechanism is improbable, since fluorenylidene reacts faster with alcohols than with ethers, and more acid alcohols present higher reactivity. So, direct insertion was proposed as the most viable pathway. However, the new mechanism presented here can explain the observation relative to the isotopic effect, which is impossible to explain by the direct insertion mechanism. Consider the following rate constants for reaction of two alcohol molecules with one carbene molecule: $k_{H,H}$, $k_{H,D}$, $k_{D,D}$, $k_{D,H}$. The H and D atoms indicate the isotopes involved in the transition state; the first atom is relative to the first alcohol molecule (that makes the hydrogen bond with carbene), and the second atom, relative to the second alcohol molecule. The relation $k_{H,H}/k_{D,D}$ is the kinetic isotopic effect. However, the product isotopic effect also will depend on $k_{H,D}$ and $k_{D,H}$, so these properties cannot be equal. Once more, the new mechanism gives a single explanation to experimental observations.

A third experimental provocative fact was reported by Scaiano et al.[38] and by Moss et al.[17] in the study of the reaction of *p*-anisylchlorocarbene and phenylchlorocarbene with methanol and *tert*-butyl alcohol. They have not observed a first-order dependence of the rate constant on alcohol concentration and have attributed this behavior to alcohol oligomerization in the solution. The new mechanism proposed here can also explain these experiments. To attain this objective, let us write the general equations for the reaction of alcohol with carbene by the OH group catalysis mechanism in an inert solvent. The following equations describe the problem:

$$\mathrm{ROH} + \mathrm{ROH} \overset{K_1}{\rightleftharpoons} (\mathrm{ROH})_2 \tag{1}$$

$$(\mathrm{ROH})_2 + \mathrm{CXY} \overset{K_2}{\rightleftharpoons} \mathrm{MS1} \tag{2}$$

$$\mathrm{MS1} \xrightarrow{k_3} \mathrm{ROCHXY} + \mathrm{ROH} \tag{3}$$

It is important to emphasize that steps 1 and 2 are equilibria, because the formation of these weakly bound complexes is diffusion controlled, i.e., very fast. Defining C_{ROH} and C_{CXY} as the total concentration of alcohol and carbene, respectively, and considering $C_{\mathrm{ROH}} \gg C_{\mathrm{CXY}}$, the following equations can be derived:

$$\frac{\mathrm{d}C_{\mathrm{CXY}}}{\mathrm{d}t} = -k_{\mathrm{obs}} C_{\mathrm{CXY}} \tag{4}$$

$$k_{\mathrm{obs}} = \frac{K_1 K_2 k_3 [\mathrm{ROH}]^2}{1 + K_1 K_2 [\mathrm{ROH}]^2} \tag{5}$$

$$[\mathrm{ROH}] = \frac{-1 + \sqrt{1 + 8K_1 C_{\mathrm{ROH}}}}{4K_1} \tag{6}$$

where [ROH] is the free alcohol concentration. These equations can be simplified, and we can identify three general situations.

Case 1:

$$1 \gg 8K_1 C_{\mathrm{ROH}} \qquad 1 \gg K_1 K_2 [\mathrm{ROH}]^2$$

The rate constant simplifies to

$$k_{\mathrm{obs}} = K_1 K_2 k_3 C_{\mathrm{ROH}}{}^2 \tag{7}$$

This situation occurs when there is a low concentration of alcohol or when its association constant (K_1) is low. Thus, practically all alcohol is free, and the rate constant is second order in total alcohol concentration. Also, in this regime, we should observe a negative activation energy, because the product $K_1K_2k_3$ has a negative E_a Arrhenius parameter. With the data for CCl_2 addition to water we will have $E_a = -5.5$ kcal/mol.

Case 2:

$$1 \ll 8K_1 C_{\mathrm{ROH}} \qquad 1 \gg K_1 K_2 [\mathrm{ROH}]^2$$

We will have

$$k_{\mathrm{obs}} = \frac{1}{2} K_2 k_3 C_{\mathrm{ROH}} \tag{8}$$

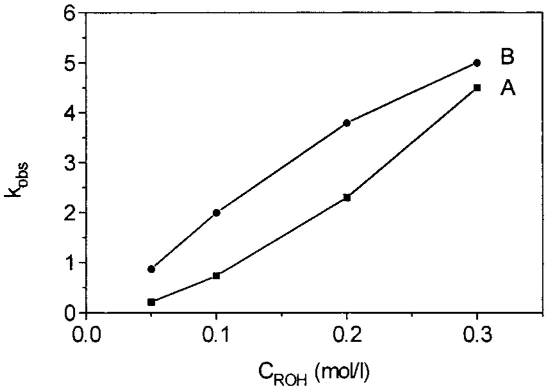


Figure 3. Pseudo first-order rate constant (k_{obs}) as a function of total alcohol concentration (C_{ROH}): (A) considering $K_1 = 1.0$ mol^{-1} L, $K_2 = 0.1$ mol^{-1} L, and $k_3 = 10^7$ s^{-1} (k_{obs} in units of 10^{-4} s^{-1}) (B) Considering $K_1 = 10.0$ mol^{-1} L, $K_2 = 10.0$ mol^{-1} L, and $k_3 = 10^7$ s^{-1} (k_{obs} in units of 10^{-6} s^{-1}).

This situation corresponds to high association of alcohol but low formation of the MS1 complex. The rate constant is linear in total alcohol concentration.

Case 3:

$$1 \ll K_1 K_2 [\mathrm{ROH}]^2$$

results in the following equation:

$$k_{\mathrm{obs}} = k_3$$

This case occurs when the carbene is completely in the MS1 form and consequently the rate constant reaches its maximum value. The rate constant is not dependent on the alcohol concentration, and we will have a positive activation energy (E_a). For the present case, $E_a = 3.46$ kcal/mol. In addition, we can make a combination of these cases. For example, at a low alcohol concentration, we can observe case 1, but increasing the concentration will change it to case 2. In an analogous form, we can have case 2 in a medium alcohol concentration and case 3 when the concentration is higher.

Now, let us present a possible explanation for the observations reported by Scaiano et al.[38] They have shown that the observed pseudo-first-order rate constant for the reaction of *p*-anisylchlorocarbene and phenylchlorocarbene with methanol and *tert*-butyl alcohol is not first order in relation to alcohol concentration. The curve $k_{\mathrm{obs}}C_{\mathrm{ROH}}$ presents a positive curvature for the reaction with methanol, while for *tert*-butyl alcohol the curvature is negative. An analysis of eqs 4−6 and the three cases discussed above show that the form of the curve depends on the K_1 and K_2 constants, i.e., on the alcohol association and the formation of the complex MS1. Let us consider two sets of reasonable values for these constants. For the set A the constants K_1 and K_2 can be fixed respectively at 1.0 and 0.10, and for the set B the constant K_1 and K_2 will be assumed to have the value of 10.0. The value of k_3 calculated in the present work is about 10^7. With these values, we can calculate the $k_{\mathrm{obs}}C_{\mathrm{ROH}}$ curve using eqs 4−6. The results are in Figure 3. For set A the curvature is positive, as observed for methanol in acetonitrile, where we expect a low alcohol association. For set B the curvature is negative, as observed for the *tert*-butyl alcohol in isooctane, where the association and the formation of the MS1 complex is higher. In addition, the observed rate constant (k_{obs}) for both cases is within the range 10^4 to 10^6 s^{-1}. This is about the same order that was observed for methanol and *tert*-butyl alcohol for a concentration around 0.10 mol/L. Again, the new mechanism proposed here is able to reproduce the experimental observations.

It is important to say that the new mechanism was shown to occur for the reaction of CCl_2 with H_2O, and its generalization is just speculation, although a very reasonable one. Nevertheless, its ability to provide a general explanation for the reaction of carbenes with alcohols is remarkable, and the present results should encourage experimental workers to investigate the kinetic behavior predicted by this mechanism for the various systems involving reactions of carbenes with alcohols.

IV. Conclusion

We have investigated the reaction of dichlorocarbene with two water molecules through a mechanism where a cyclic transition structure is formed. This mechanism presents a high rate constant, and it can explain a series of facts observed for reactions of carbenes with alcohols. Thus, we propose that this new mechanism, named OH group catalysis mechanism, is operating for the reaction of CCl_2 with H_2O, and possibly may be involved in many reactions of carbenes with OH groups.

Acknowledgment. We thank the Consellho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), and the Programa de Apoio ao Desenvolvimento Científico e Tecnológico (PADCT II) for supporting this research project.

References and Notes

(1) Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15.

(2) Pliego, J. R., Jr.; De Almeida, W. B. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1881.

(3) Gonzalez, C.; Restrepo-Cossio, A.; Marques, M.; Wiberg, K. B. *J. Am. Chem. Soc.* **1996**, *118*, 5408.

(4) Pliego, J. R., Jr.; De Almeida, W. B. *J. Phys. Chem.* **1996**, *100*, 12410.

(5) Pliego, J. R., Jr.; De Almeida, W. B. *Chem. Phys. Lett.* **1996**, *249*, 136.

(6) Pliego, J. R., Jr.; De Almeida, W. B. *J. Chem. Phys.* **1997**, *106*, 3582.

(7) Yamaguchi, Y.; Schaefer, H. F., III; Alberts, I. L. *J. Am. Chem. Soc.* **1993**, *115*, 5790.

(8) Pliego, J. R., Jr.; De Almeida, W. B. *J. Braz. Chem. Soc.* **1998**, *9*, 181.

(9) Volatron, F.; Anh, N. T.; Jean, Y. *J. Am. Chem. Soc.* **1983**, *105*, 2359.

(10) Pliego, J. R., Jr.; De Almeida, W. B. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2365.

(11) Soundarajan, N.; Jackson, J. E.; Platz, M. S.; Liu, M. T. H. *Tetrahedron Lett.* **1988**, *29*, 3419.

(12) Chateauneuf, J. E.; Liu, M. T. H. *J. Am. Chem. Soc.* **1991**, *113*, 6585.

(13) Platz, M. S.; Olson, D. R. *J. Phys. Org. Chem.* **1996**, *9*, 689.

(14) Admasu, A.; Gudmundsdottir, A. D.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 3832.

(15) Wang, J. L.; Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popik, V. *J. Am. Chem. Soc.* **1995**, *117*, 5477.

(16) Kirmse, W.; Meinert, T.; Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8918.

(17) Moss, R. A.; Shen, S.; Wlostowski, M. *Tetrahedron Lett.* **1988**, *29*, 6417.

(18) Belt, S. T.; Bohne, C.; Charette, G.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 2200.

(19) Chateauneuf, J. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1437.

(20) Kirmse, W.; Kilian, J.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 6399.

(21) Pliego, J. R., Jr.; França, M. A.; De Almeida, W. B. *Chem. Phys. Lett.* **1998**, *285*, 121.

(22) Dunning, T. H.; Hay, P. J. In *Methods of Electronic Structure Theory*; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977.

(23) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(24) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(25) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(26) Curtiss, L. A.; Carpenter, J. E.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1992**, *96*, 9030.

(27) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(28) Nobes, R. H.; Bouma, W. J.; Radom, L. *Chem. Phys. Lett.* **1982**, *89*, 497.

(29) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.2; Gaussian, Inc.: Pittsburgh, PA, 1995.

(30) Breneman, C. M.; Wiberg, K. B. *J. Comput. Chem.* **1990**, *11*, 361.

(31) Jorgensen, W. L.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1988**, *110*, 1657.

(32) Jorgensen, W. L.; Briggs, J. M.; Contreras, M. L. *J. Phys. Chem.* **1990**, *94*, 1683.

(33) Jorgensen, W. L.; Ravimohan, C. *J. Chem. Phys.* **1985**, *83*, 3050.

(34) Jorgensen, W. L. *BOSS*, version 3.5; Yale University: New Haven, CT, 1995.

(35) Bethell, D.; Newall, A. R.; Whittaker, D. *J. Chem. Soc. B* **1971**, 23.

(36) Zupancic, J. J.; Crase, P. B.; Lapin, S. C.; Schuster, G. B. *Tetrahedron* **1985**, *41*, 1471.

(37) Olson, D. R.; Platz, M. S. *J. Phys. Org. Chem.* **1996**, *9*, 759.

(38) Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.