The Kinetics of the Reactions of C_2 ($a^3\Pi_u$) with Alcohols

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The reactions of C_2 ($a^3\Pi_u$) radicals with a series of alcohols have been studied at about 6.5 Torr total pressure and room temperature using the pulsed laser photolysis/laser-induced fluorescence technique. The relative concentration of C_2 ($a^3\Pi_u$) radicals, which are generated via the photolysis of C_2Cl_4 with the focused output from the fourth harmonic of a Nd:YAG laser (266 nm), was monitored by laser-induced fluorescence (LIF) in the (0, 0) band of the C_2 ($d^3\Pi_g \leftarrow a^3\Pi_u$) transition at 516.5 nm. Under pseudo-first-order conditions, we measured the time evolution of C_2 ($a^3\Pi_u$) and determined the rate constants for reactions of C_2 ($a^3\Pi_u$) with alcohols. The rate constants increase linearly with the number of C atoms in the alcohols. All of them are larger than those for reactions of C_2 ($a^3\Pi_u$) with alkanes (C_1-C_5). Based on the bond dissociation energy and linear free energy correlations, we believe the reactions of C_2 ($a^3\Pi_u$) with alcohols proceed via the mechanism of hydrogen abstraction. The experimental results show that the H-atom on the C−H bonds is activated at the presence of the OH substituent group in the alcohol molecule. The theoretical calculations for the reaction of C_2 ($a^3\Pi_u$) with methanol also support these hypotheses.

Introduction

Diatomic carbon molecules are found in a very wide variety of sources, such as comets, interstellar clouds, the sun, and stellar atmospheres.[1−4] It plays an important role in astrophysics as well as in many chemical systems in which reactions of hydrocarbons are involved.[5−7] In addition to being one of the simplest diatomic molecules, C_2 is one of the few small molecules that have two low lying electronic states: the ground $X^1\Sigma^+{}_g$ state and the metastable triplet state, $a^3\Pi_u$. These states are separated by only 610 cm^{-1} (1.7 kcal/mol). C_2 ($a^3\Pi_u$) and C_2 ($X^1\Sigma^+{}_g$) states can be observed directly using the LIF method via the Swan bands and the Phillips bands of C_2, respectively.[8] This provides the opportunity to study the elementary process of C_2 reactions with small molecules in the gaseous phase involving two electronic and spin states. The rate coefficients and mechanisms for C_2 reactions are of major interest. Nevertheless, the detailed kinetic behavior of the radical has attracted scientists for many years, as C_2 radicals could not be prepared in a well-controlled experimental condition. Nowadays, that diatomic carbon can be easily prepared by using either IR multiphoton dissociation (MPD)[9−13] or UV laser photolysis,[14−16] and C_2 has been the subject of spectroscopic, kinetic, photodissociation, and theoretical studies to elucidate its structure, reactivity, and energy state.[17−20] Reisler, Mangir, and Wittig[10−13] produced C_2 by CO_2 laser IR photolysis of C_2H_3CN, C_2HCl_3, or C_2H_4 and made observations on both the C_2 ($X^1\Sigma^+{}_g$) and the C_2 ($a^3\Pi_u$) molecules. Some rate coefficients for the removal of C_2 ($X^1\Sigma^+{}_g$ and $a^3\Pi_u$) and the C_2 ($a^3\Pi_u$) ↔ C_2 ($X^1\Sigma^+{}_g$) intersystem crossing were reported. Pasternack et al.[14,15] studied the reactions of C_2 ($a^3\Pi_u$) with hydrogen and small hydrocarbons, in which C_2 ($a^3\Pi_u$) is produced by multiphoton UV photolysis using a focused excimer laser, and either hexafluorobutyne-2, photolyzed at 193 nm, or benzene, photolyzed at 248 nm, is used as the precursor molecules. Recently, Fontijn's group studied the temperature dependence of the reactions of C_2 ($a^3\Pi_u$) with O_2 and NO in a high-temperature photochemistry reactor by the 193 nm multiphoton photolysis of C_2Cl_4.[21,22]

Although quite an extensive data set of the reactions of C_2 ($X^1\Sigma^+{}_g$ and $a^3\Pi_u$) has been accumulated hitherto, little has been reported on the rate constants for reactions of C_2 ($a^3\Pi_u$) with alcohols in the gas phase. In the present paper, we will report the values of the bimolecular reaction rate constants for reactions of the C_2 ($a^3\Pi_u$) radical with selected alcohols (C_1-C_5) in the presence of excess Ar buffer gas at about 6.5 Torr total pressure and room temperature using the pulsed laser photolysis/laser-induced fluorescence technique. The hydrogen abstraction mechanism for these reactions is discussed based on the bond dissociation energy and linear free energy correlations.

Experimental Section

The pulsed laser photolysis/laser-induced fluorescence experiments were performed in a stainless steel flow reactor in the present work, which is basically similar to those described by other authors in the literature.[23,24] Briefly, triplet C_2 radicals were generated via the selected polyatomic molecule photolysis with the focused output from the fourth harmonic of a Nd:YAG laser (New wave) at 266 nm. The typical pulse energy and time jitter of the photolysis laser are 5 mJ and 2 ns. A 50 cm focal length quartz lens serves to focus the beam at the center of the reaction cell. A second Nd:YAG laser (Spectra physics, GCR-170, repetition rate of 10 Hz) with a pulse width of 8 ns and jitter of 2 ns pumps a dye laser (Sirah) at 355 nm. The excitation laser beam and the photolysis laser overlap in the reaction cell collinearly in a counter propagating way. The dye laser output at 516.5 nm, about 2.0 mJ/pulse, pumps the (0, 0) vibronic band of the C_2 ($d^3\Pi_g \leftarrow a^3\Pi_u$) electronic transition. To minimize the scattered light, the laser beams passed through a system of special light baffles. The fluorescence was monitored on the (0, 1) band of the C_2 ($d^3\Pi_g \rightarrow a^3\Pi_u$) transition at 563.5 nm and

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collected by a lens system, passed through an interference filter (0.7 nm FWHM), and then focused onto a photomultiplier (R928, Hamamatsu). The output of the photomultiplier was fed to a digital storage oscilloscope (TDS380, Tektronix) or a transient digitizer and then averaged with a computer data acquisition system. The fluorescence signals were averaged over 256 laser pulses. The delay time between the photolysis laser and the probe dye laser varies from zero to several hundred microseconds controlled by a digital delay generator (Stanford Research DG535).

In a typical experiment, a premixed gas sample contained a suitable polyatomic molecule as the C_2 radical precursor in Ar, the reactant alcohol mixed with Ar, and pure Ar as buffer gas. The gas sample was supplied from cylinders through a stainless steel line and controlled by an individually calibrated mass flow controller (D07-7A/2M, Beijing), which slowly passed through the fluorescence chamber. Typical precursor C_2Cl_4 concentrations are about 6.0×10^{13} molecule cm^{-3}. The alcohol concentrations ranged from 1.0×10^{14} to 1.0×10^{15} molecule cm^{-3}. The total pressure in the chamber was about 6.5 Torr, and the partial pressure of precursor C_2Cl_4 was 1.8 mTorr. The initial C_2 ($a^3\Pi_u$) radicals generated from the precursor are rotationally hot. The Ar buffer gas was included in the reaction mixture to relax the nascent quantum state distributions of both reactants and C_2 ($a^3\Pi_u$) radicals and to slow the diffusion rate of molecules out of the laser probe region in the reaction cell. The rate coefficients are measured after the C_2 ($a^3\Pi_u$) radical is rotationally cooled to room temperature, which occurred within 8 μs.

Gas sources and purities were C_2Cl_4 (Shanghai, $\geq$97%), methanol (Shanghai, $\geq$99.5%), ethanol (Shanghai, $\geq$99.5%), propanol (Shanghai, $\geq$99.0%), butanol (Shanghai, $\geq$99.5%), and pentanol (Shanghai, $\geq$99.5%). All gases were degassed by repeated freeze−pump−thaw cycles in liquid nitrogen. Ar (Nanjing gas 99.999%) was used without further purification.

Results

The multiphoton photolysis of C_2Cl_4 at 266 nm results in the formation of both ground and electronically excited C_2 radicals. Additionally, higher vibrational levels of the C_2 ($a^3\Pi_u$) state are also produced. Thus, upon monitoring the temporal behavior of C_2 ($a^3\Pi_u$) ($\upsilon = 0$), it was observed that an initial rise in signal occurred followed by a slow decay. This initial rise was due to vibrational relaxation. All kinetic data were taken after these initial relaxation effects were no longer observed. In all cases, the time evolution of C_2 followed an exponential decay for at least two lifetimes.

Both C_2 ($a^3\Pi_u$) and C_2 ($X^1\Sigma^+{}_g$) are produced by the 266 nm photolysis of C_2Cl_4. Thus, quenching and collisionally induced intersystem crossing may occur in the reaction system. As for the small alcohols reactants, which are singlet molecules and composed of light atoms, spin conservation rules are expected to hold. The quenching and collisionally induced intersystem crossing (C_2 ($a^3\Pi_u$) $\leftrightarrow$ C_2 ($X^1\Sigma^+{}_g$)) is much slower than reactions and can be neglected.[13]

The intensity of the LIF signal from C_2 ($d^3\Pi_g \leftarrow a^3\Pi_u$) was taken as a relative measure of the C_2 ($a^3\Pi_u$) concentration. Following initial relaxation effects, the LIF intensity, I, decayed exponentially approximately as a function of the delay time, t, after the photolysis pulse ($t > 8\mu s$). The signal is fitted by least-squares to the equation

$$I = A \exp(-k_1 t)$$

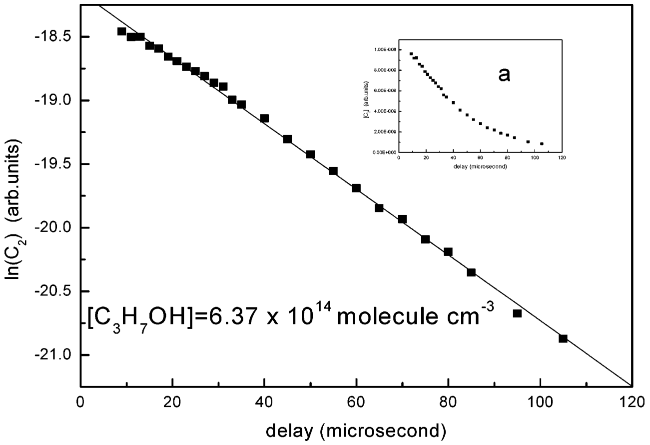

Figure 1. Typical plots of C_2 ($a^3\Pi_u$) intensity versus the delay time between the photolysis laser (266 nm) and probe laser (516.5 nm) at 6.5 Torr total pressure and 298 K. The solid line is the result of weighted linear least-squares fits to the data. (a) is the raw data.

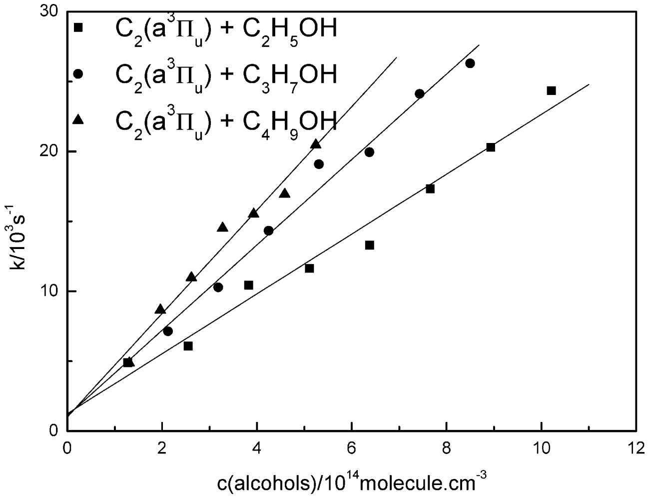

Figure 2. Plots of pseudo-first-order decay constant k' versus the alcohols concentration in the presence of excess Ar buffer gas at 6.5 Torr total pressure and 298 K. The solid lines are the results of weighted linear least-squares fits to the data.

where k_1 is the pseudo-first-order decay rate constant for the C_2 LIF due to all loss processes, such as reaction and diffusion out of the probe beam.

Typical plots of the natural logarithm of the C_2 LIF signal are shown in Figure 1. The decay rate constant k_1 increased proportionally to the concentration of added alcohol reactant. These pseudo-first-order rate constants determined for a particular temperature and total pressure were fitted by least-squares to the equation

$$k_1 = k[R] + k_n$$

where k is the bimolecular rate constant for the reaction of C_2 ($a^3\Pi_u$) with reactant R, and k_n is the loss rate constant for C_2 ($a^3\Pi_u$) due to reaction and diffusion in the absence of alcohol. Typical plots of k_1 versus [R] are shown in Figure 2 for R = C_2H_5OH, C_3H_7OH, C_4H_9OH. The rate constants of reactions C_2 ($a^3\Pi_u$) with the selected alcohols (C_1-C_5) at 298 K are summarized in Table 1. The errors listed are 1σ.

Discussion

It is readily apparent that the reactions of C_2 ($a^3\Pi_u$) with alcohols are very rapid. To our knowledge, no previous rate

TABLE 1: Rate Constants for O (^3P), OH, and C_2 ($a^3\Pi_u$) Reactions with Alcohols and Alkanes at Room Temperature; Uncertainties Are $\pm 1\sigma$

compound	k ($^3C_2$) × $10^{11\,a}$	$k_{O(^3P)}$ × $10^{15\,a,b}$ [27,33]	k_{OH} × $10^{13\,a,b}$ [27,35,36]
methanol	0.38 ± 0.03	7.7934	9.22
ethanol	2.14 ± 0.13	55.7	30.85
propanol	3.05 ± 0.17		54.15
butanol	4.89 ± 0.22	123	79.35
pentanol	10.20 ± 0.49		
methane	$<2 \times 10^{-3}$ [25]	0.017	0.08
ethane	0.125 ± 0.07[25]	0.91	2.8
propane	1.34 ± 0.07[25]	15	19
butane	3.19 ± 0.15[25]	31	30
pentane	6.65 ± 0.38[25]	58	50

[a] In units cm^3 $molecule^{-1}$ s^{-1}. [b] Where more than one literature value is available, the mean is given.

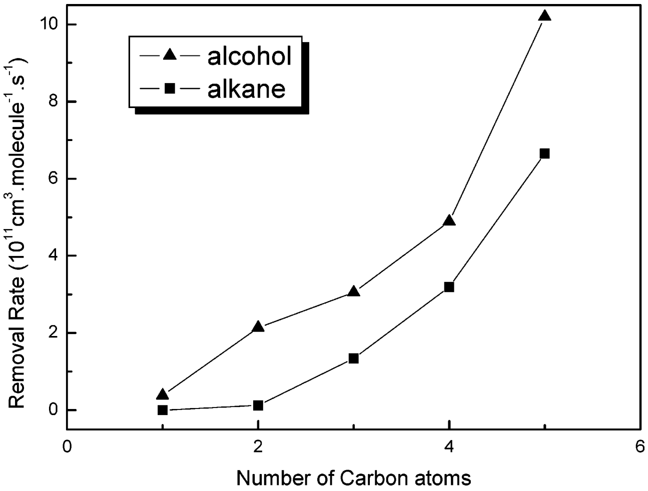

Figure 3. The dependence of the experimental rate constants for removal of C_2 ($a^3\Pi_u$) by alcohols and alkanes on the number of C atoms in alcohol and alkane molecules.

constants have been measured for the reaction of C_2 ($a^3\Pi_u$) with alcohol molecules. In fact, chemical reaction is a complicated process. We could not obtain the precise mechanism by only depending on the removal rate constants of C_2 ($a^3\Pi_u$). Yet we may achieve some reasonable conclusions by qualitative analysis.

In our previous work,[25] the rate constants for the reactions of C_2 ($a^3\Pi_u$) with alkanes have been studied. To compare these results, the rate constants at room temperature for the reactions of C_2 ($a^3\Pi_u$) with alcohols and alkanes are listed in Table 1 and shown in Figure 3, respectively. As shown in Figure 3, the C_2 ($a^3\Pi_u$) removal rate constants for alcohols are larger than those for the corresponding alkanes, and the two sequences both increase monotonically with the C-atoms number contained in the alcohol and alkane molecules. For the reactions of C_2 ($a^3\Pi_u$) with alkanes, the hydrogen abstraction mechanism is confirmed.[25] We will argue here that the reactions of C_2 ($a^3\Pi_u$) with alcohols probably proceed also via the same mechanism. From the view of structure active relationship (SARs) theory,[26-28] if reactive species such as C_2 ($a^3\Pi_u$) are known to react with a series of organic compounds via a similar mechanistic pathway, it may be expected that there will exist relationships between the structural and physical properties of these molecules and their reactivity. We will discuss this below in detail. Moreover, ab initio calculations for the reaction of C_2 ($a^3\Pi_u$) with methanol support that the hydrogen abstraction is dominant.

(a) BDE Correlation. Many experimental studies indicate a general trend in the reactivity of radical and molecule reaction. The rate constants for the addition reaction correlate with ionization potential (IP), while for the abstraction reaction they correlate with the bond dissociation energy (BDE).[26-28] For the hydrogen abstraction mechanism, the rate constants increase with decreasing bond dissociation energy at room temperature. In our previous studies,[25] the rate constants for the reaction of C_2 ($a^3\Pi_u$) with the primary, secondary, and tertiary hydrogen of alkanes increase with the decrease of the BDE. The correlation of rate constants with BDE was confirmed. In current studies, the rate constants are larger than that for the accordingly alkanes. The marked variation that can be considered is the alcohols are formed by substituting an OH group instead of an H atom in the alkanes. In fact, the H-atom on the OH group of the alcohol is very difficult to abstract because the bond dissociation energy of the O−H bond in the alcohol molecule is so large. The value is 438 ± 3 kJ/mol, which is near the 439.3 ± 0.1 kJ/mol of the C−H bond in the methane.[29,30] From ref 25, we know that the H-atom of the methane is almost impossible to abstract ($<2 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1}). However, due to the induction of the OH substituent group, the H-atoms on the C−H bonds are activated in the alcohol molecule. Considering the methanol molecule, the bond dissociation energy of the C−H bonds is 401.9 ± 0.6 kJ/mol,[31] which is smaller than the bond dissociation energy of the C−H bonds in the methane (439.3 ± 0.1 kJ/mol). Accordingly, the bond dissociation energy of the secondary hydrogen in the alcohol molecules (401.4 ± 1.5 kJ/mol) is also smaller than that in the alkane molecules (413 ± 2 kJ/mol).[31,32] So the H-atom on the C−H bonds in the alcohol molecule is easier to abstract than that in the alkane molecule. It is in qualitative agreement with the experimental results; the rate constants for the C_2 ($a^3\Pi_u$) reactions with alcohols are larger than those for alkanes. This indicates the reactions of C_2 ($a^3\Pi_u$) with alcohols may proceed via the hydrogen abstraction mechanism.

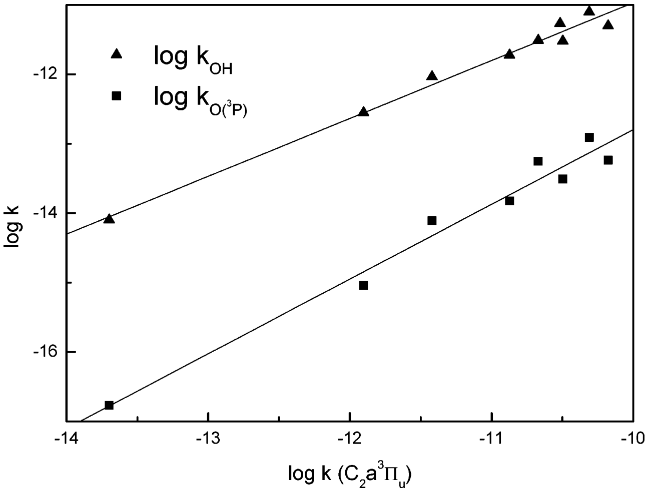

Figure 4. Linear free energy correlation of the rate constants for C_2 ($a^3\Pi_u$), O (^3P), and OH radical react with the small alcohols and alkanes. The O (^3P) and OH reactions are known to proceed via hydrogen abstraction. The line is the least-squares best fit.

(b) LFE Correlation. Additional support is provided for the postulated hydrogen abstraction mechanism for reactions of C_2 ($a^3\Pi_u$) with alcohols and alkanes from the linear free energy correlations. In view of Levin etc.,[26] if reactive species are known to react with a series of organic compounds via a similar mechanistic pathway, the rate constants linearly correlate with the free energy. Such as the O (^3P) and OH reactions, it has been well established that O (^3P) and OH radical react with alcohols and alkanes by abstraction. So plots of log k (O^3P)

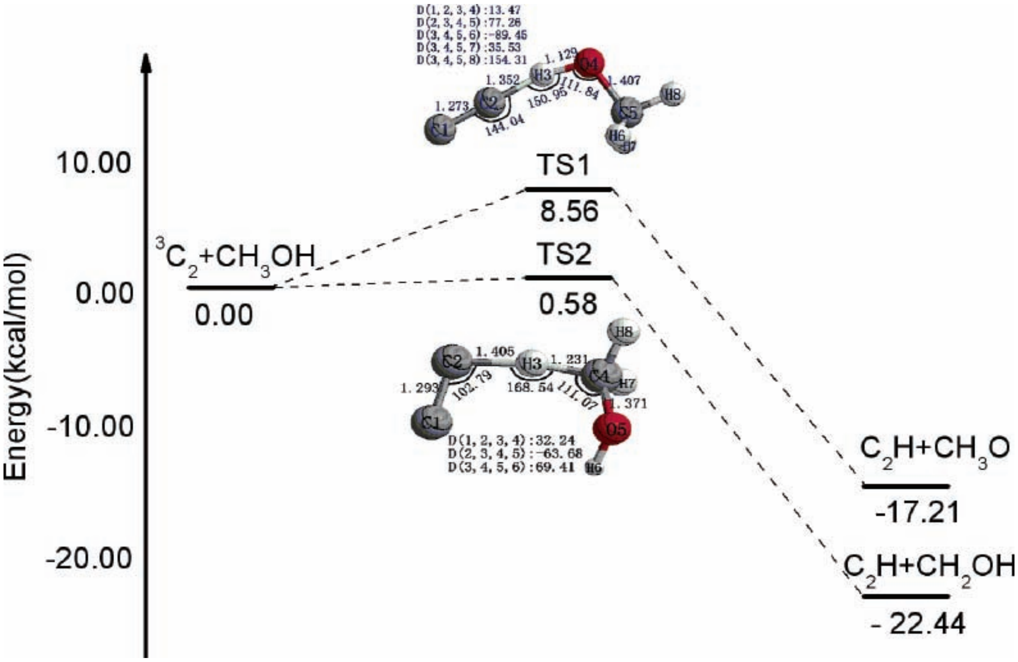

Figure 5. Schematic energy (in kcal mol^{-1}) relative to C_2 ($a^3\Pi_u$) + CH_3OH. The energy was computed at the G3MP2 level of theory.

and log *k* (OH) versus log *k* ($^3C_2$) should be linear. We consider that the reactions of C_2 ($a^3\Pi_u$) with alcohols and alkanes are analogous to O (^3P) and OH reaction mechanisms. The available rate constants for the O (^3P) and OH reactions are also listed in Table 1. Plots of log *k* (O^3P) and log *k* (OH) versus log *k* ($^3C_2$) are linear (see Figure 4) as expected for reactions proceeding via the same hydrogen abstraction mechanism.[14,26] From ref 26, for abstraction reactions of O (^3P) and OH, the LFE correlation is significantly better than the BDE method, which appears to have more qualitative than quantitative usefulness in estimating rate constants.

(c) C_2 ($a^3\Pi_u$) + CH_3OH Calculation. To obtain insight into the reaction mechanism for the reaction of C_2 ($a^3\Pi_u$) with alcohols, ab initio calculation was performed on the reaction of C_2 ($a^3\Pi_u$) with CH_3OH as the guide. All calculations were implemented using Gaussian 03 program. Geometries of reactants, products, intermediates (IM), and transition state (TS) structures involved in the reaction of C_2 ($a^3\Pi_u$) + CH_3OH were optimized at the MP2(full)/6-311++G(d,p) level. Harmonic vibration frequencies evaluated at the MP2(full)/6-311++G(d,p) level are listed in Table 2. The optimized reactant and product species as well as intermediate species are found to have all positive frequencies, indicating that each of these species is a local minimum on the potential energy surface. The optimized transition state configuration involved in the reaction possesses an imaginary frequency, indicating a saddle point on the potential surface for the located transition state configuration. The overall energy diagram obtained at the G3MP2[37] level for the reaction is presented in Figure 5, which describes the reaction mechanism clearly.

When the C_2 ($a^3\Pi_u$) approaches the CH_3OH molecule, two hydrogen abstraction channels may exist: the C_2 ($a^3\Pi_u$) abstracts the H-atom from the O−H bond and from the C−H bond, as shown in Figure 5. The C_2 ($a^3\Pi_u$) abstracting the H-atom from the O−H bond produces C_2H and CH_3O via TS1 whose energy is 8.56 kcal mol^{-1} higher than that of the reactant. This barrier is too high to get across at room temperature. The contribution of this channel is minimal. Yet the C_2 ($a^3\Pi_u$) abstracting the H-atom from the C−H bond produces C_2H and CH_2OH via TS2 almost without barrier (0.58 kcal mol^{-1}). This process easily goes ahead. The association of a transition state to the corresponding reactants and products was examined and confirmed by running the IRC job[38,39] to follow the reaction paths downhill in both forward and reverse directions, and the results are summarized in Figure 5. The barrier is higher for the C_2 ($a^3\Pi_u$) abstracting the H-atom from the O−H band than that from the C−H bond. This is in good agreement with the bond dissociation energy (BDE) correlation theory. The calculation results indicate the reaction of C_2 ($a^3\Pi_u$) with CH_3OH proceeds via the hydrogen abstraction mechanism.

TABLE 2: Harmonic Vibrational Frequency (cm^{-1}) Calculated at the MP2(full)/6-311++G(d,p) Level of Theory for Various Species Involved in C_2 ($a^3\Pi_u$) + CH_3OH[a]

species	vibrational frequencies
TS1	2038.41i, 107.08, 146.41, 223.73, 285.16, 640.24, 1061.82, 1162.87, 1192.58, 1371.15, 1486.06, 1502.91, 1547.72, 1973.49, 2286.24, 3069.40, 3171.35, 3177.22
TS2	424.85i, 70.03, 126.95, 185.70, 284.03, 453.25, 1022.40, 1126.06, 1171.32, 1379.47, 1442.78, 1480.16, 1527.38, 2059.45, 2269.46, 3105.05, 3211.00, 3758.78
C_2 ($a^3\Pi_u$)	1672.58
CH_3OH	312.96, 1078.07, 1099.75, 1196.88, 1380.76, 1508.82, 1516.69, 1532.56, 3060.67, 3130.77, 3196.44, 3917.96
C_2H	839.53, 839.53, 2466.88, 3579.38
CH_2OH	413.09, 857.74, 1155.78, 1287.70, 1483.00, 1626.85, 3287.20, 3424.64, 4122.63
CH_3O	820.16, 1108.95, 1211.69, 1583.63, 1593.61, 1666.48, 3181.79, 3248.28, 3264.69

[a] i represents imaginary frequency.

On the basis of the above analysis, we conclude that the reaction of C_2 ($a^3\Pi_u$) with small alcohols proceeds via the mechanism of hydrogen abstraction. The H-atom on the C−H bonds is activated by the presence of the OH substituent group in the alcohol molecule. Future theoretical calculations and experimental studies on reactions of C_2 ($a^3\Pi_u$) with alcohols will be helpful to better understand these processes.

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