Article

Photooxidation of Di-*tert*-butyl Malonate in the Presence and Absence of Nitrogen Dioxide

Diana Henao, Walter Peláez, Gustavo A. Argüello, and Fabio E. Malanca*

Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC) CONICET − Departamento de Fisicoquímica, Facultad de Ciencias Químicas (Universidad Nacional de Córdoba), Ciudad Universitaria (X5000HUA), Córdoba, República Argentina

ABSTRACT: The rate constant for the reaction of di-*tert*-butyl malonate (DTBM) with chlorine atoms in the gas phase was measured using cyclohexane and pentane as references. The measurements lead to a value of $(1.5 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The subsequent photo-oxidation mechanism of DTBM in the absence and presence of nitrogen dioxide was investigated. The main carbonated products identified in the first case were acetone, formic acid, carbon monoxide, and carbon dioxide. The addition of nitrogen dioxide lead besides to the formation of $(CH_3)_3CC(O)OONO_2$ and $(CH_3)_3CONO_2$. The proposed photo-oxidation mechanism was supported both experimentally and computationally. The results reveal that the $(CH_3)_3COC(O)CH_2C(O)OC(CH_3)_2O^{\bullet}$ radical formed reacts

according to two competitive reactions: decomposition to yield acetone and $(CH_3)_3COC(O)CH_2C(O)O^{\bullet}$ radical $55 \pm 2\%$, and migration of the H atom of the methylene group to the terminal oxygen atom $40 \pm 3\%$.
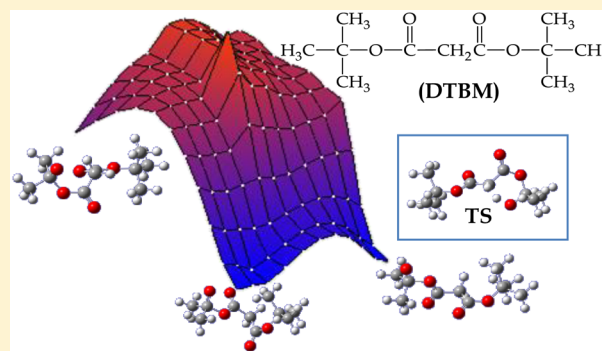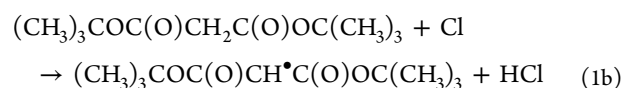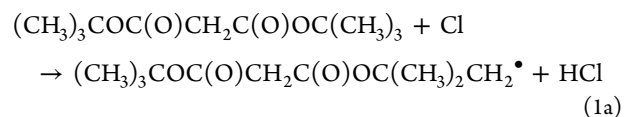
INTRODUCTION

Malonic acid diesters are widely used in the chemical industry as building block intermediates for the synthesis of a variety of organic chemicals. The end products of the different processes in which malonates are used include pharmaceuticals, agrochemicals, vitamins, fragrances, and dyes.

To improve the knowledge of the atmospheric chemistry of malonic acid diesters, we have determined the rate coefficient of chlorine atoms (used as surrogate for hydroxyl radicals) with di-*tert*-butyl malonate, $(CH_3)_3COC(O)CH_2C(O)OC(CH_3)_3$ (DTBM), and its photo-oxidation mechanism in both the presence and absence of nitrogen dioxide in gas phase.

Reported values of the rate coefficients of chlorine atoms for dibasic esters available in the bibliography $[(6.8 \pm 0.9), (1.9 \pm 0.3),$ and $(6.1 \pm 0.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} for $CH_3OC(O)(CH_2)_nC(O)OCH_3,$), with $n = 2$, 3, and 4, respectively[1]] suggest that the rate coefficient of DTBM with chlorine atoms would also be high, on account of the presence of more attack sites (six methyl groups in the molecule).

This points to the possibility of degradation of DTBM in the atmosphere through the photo-oxidation initiated by $^{\bullet}$OH radicals and therefore the relevance of knowing its reaction mechanism and the products formed. Reaction with chlorine atoms was employed as a surrogate to mimic the $^{\bullet}$OH radical induced atmospheric oxidation. Although reaction with chlorine atoms is somewhat less selective as with $^{\bullet}$OH radicals, the subsequent chemistry is the same and thus it is a convenient method to emulate $^{\bullet}$OH radical initiated chemistry.[1]

The chlorine atoms attack to DTBM could *a priori* abstract a hydrogen in two sites of the molecule: methyl and methylene groups (reactions 1a and 1b, respectively):

$$(CH_3)_3COC(O)CH_2C(O)OC(CH_3)_3 + Cl$$
$$\rightarrow (CH_3)_3COC(O)CH_2C(O)OC(CH_3)_2CH_2^{\bullet} + HCl \quad (1a)$$

$$(CH_3)_3COC(O)CH_2C(O)OC(CH_3)_3 + Cl$$
$$\rightarrow (CH_3)_3COC(O)CH^{\bullet}C(O)OC(CH_3)_3 + HCl \quad (1b)$$

The global rate coefficients were measured in this work via relative methods using two reference gases (cyclohexane and *n*-pentane), and the values were compared with those obtained from structure−reactivity estimation methods (SAR).[2−4]

As for other organic compounds, the atmospheric degradation of DTBM involves further reactions of radicals formed in reactions 1a and 1b, with molecular oxygen leading to peroxy and oxy radicals and the ulterior formation of stable products.[5] The photo-oxidation mechanism in polluted areas with high nitrogen dioxide concentrations gives additionally the formation of nitrates and peroxynitrates, the latter being an important reservoir species of peroxy radicals and NO_2 that could be transported over large distances from polluted to unpolluted areas contributing to ozone formation.[6−8] Therefore, the photo-oxidation of DTBM in the absence and the presence of nitrogen dioxide was investigated to identify and quantify the products and to determine the reaction mechanism. The main reaction pathways were supported by

experimental results as well as by computational calculations using Gaussian 09 suite.[9]

■ EXPERIMENTAL SECTION

Chemicals. Commercially available samples of di-*tert*-butyl malonate (Sigma-Aldrich), cyclohexane (Dorwil), pentane (Dorwil), O_2 (AGA), and N_2 (AGA) were used. Chlorine (>99%) was prepared from the reaction between $KMnO_4$ and HCl and further distilled. NO_2 (>99%) was obtained from thermal decomposition of $Pb(NO_3)_2$.[10]

Procedure. The manipulation of gases was carried out in a conventional glass vacuum line equipped with two capacitance pressure gauges (0−1000 mbar, MKS Baratron; 0−70 mbar, Bell and Howell).

All photolytic experiments were carried out in a photoreactor consisting of a 5 L glass bulb, surrounded by three black lamps, that was coupled to a Fourier transform infrared spectrometer to obtain IR spectra of the progress of the reactions. Experiments were carried out by photolyzing the mixture of reactants and expanding, from time to time, a small sample into a long path infrared gas cell (optical path, 9.5 m). Spectra were recorded with a resolution of 2 cm^{-1}. Identification and quantification of reactants and products were performed by infrared spectroscopy, using reference spectra.

Mixtures were prepared by injecting, through a septum, 10 μL of DTBM (4.5×10^{-5} mol) into the photoreactor. This procedure was undertaken due to the relatively low vapor pressure at room temperature (0.22 mbar) of DTBM and was followed by further addition of chlorine (0.35 mbar) and either nitrogen (for determination of the rate coefficients) or oxygen (for photo-oxidation experiments) to reach atmospheric pressure. For the photolyses in the presence of NO_2, 0.2 mbar were added to the previous mixture. Control experiments were performed in the dark to check for losses of DTBM due to heterogeneous or dark reactions.

As already mentioned, the rate coefficient for the reaction of DTBM with chlorine atoms was determined using a relative method, employing cyclohexane and pentane as reference gases.[1,11]

Computational Details. Software Gaussian09[9] was used to compare the energy requirements of two relevant reaction paths of the photo-oxidation mechanism. The geometric parameters for reactants, transition states, and products were fully optimized using density functional theory[12] with the B3LYP functional and the 6-311+G(d,p) basis set.

■ RESULTS AND DISCUSSION

Rate Coefficients for the Gas-Phase Reactions with Cl Atoms. The rate coefficients for the reaction of chlorine atoms with DTBM were determined using cyclohexane and pentane as reference gases from eq 1[1]

$$\ln\left[\frac{DTBM_0}{DTBM_t}\right] - k_{wall}xt = \frac{k_{DTBM}}{k_{ref}}\ln\left[\frac{reference_0}{reference_t}\right] \quad (1)$$

where $[DTBM]_0$, $[DTBM]_t$, $[reference]_0$, and $[reference]_t$ indicate substrate and reference concentrations before ($t = 0$) and at time (t) of irradiation, respectively. The observed disappearance of di-*tert*-butyl malonate against those of the reference compounds are plotted according to eq 1. The former expression should be linear, with a slope (k_{DTBM}/k_{ref}) from which the rate constant of interest could be obtained. The value

of k_{wall} (which accounts for overall non photolytic processes) in typical experiments was 2.04×10^{-4} s^{-1}.

Figure 1 shows the good straight-line plots using cyclohexane and *n*-pentane as reference compounds. Their rate coefficients,
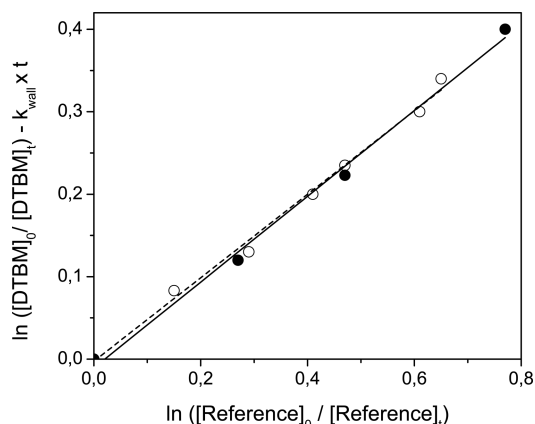

Figure 1. Kinetic data (total pressure 1000 mbar at 296 K) for the reaction of chlorine atoms with DTBM relative to cyclohexane (open circles) and pentane (solid circles).

taken form bibliography, are (2.91 and 2.75) $\times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.[13,14] The value of k_{DTBM} obtained from these plots are (1.45 and 1.54) $\times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}, respectively, leading to a mean value of $(1.5 \pm 0.1) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.

This value agrees with the rate coefficients calculated using the SAR method applied to the reactions of Cl atoms with similar molecules.[2,3] In the SAR (structure−activity relationship) method, the calculation of the overall rate constant is based on the estimation of $-CH_3$, $-CH_2-$, and $>CH-$ group rate constants. The values reported by Notario[15] for rate constants, $k_{prim} = 3.32 \times 10^{-11}$, $k_{sec} = 8.34 \times 10^{-11}$, and $k_{tert} = 6.09 \times 10^{-11}$ (all in units of cm^3 $molecule^{-1}$ s^{-1}) and group parameters $F(-CH_3) = 1.00$, $F(-CH_2-) = F(>CH-) = F(>C<) = 0.79$, $F(-CO) = 0.04$, and $F(C(O)O-) = 0.05$ were taken as such and used, when appropriate, in our system. These $[6 \times 3.32 \times 10^{-11} \times (0.79)^1 + 1 \times 8.34 \times 10^{-11} \times (0.04)^2]$ lead to a value for the estimation of the rate coefficient of DTBM with chlorine atoms of 1.57×10^{-10} cm^3 $molecule^{-1}$ s^{-1}, which implicitly carries a contribution for the attack to secondary carbon atoms of less than 1%, and therefore Cl atoms react almost exclusively with methyl groups.

This value is higher than the ones corresponding to *tert*-butyl acetate $((CH_3)_3COC(O)CH_3$, (1.6 ± 0.3), (2.4 ± 0.3), $(1.6 \pm 0.1) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} reported by Langer et al, Notario et al., and Xing et al., respectively)[15−17] and dimethyl succinate, $CH_3OC(O)(CH_2)_2C(O)OCH_3$ ($k = (6.8 \pm 0.9) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}), as expected on account of the presence of more reactive methyl groups in the DTBM.

Photo-oxidation Mechanism in the Absence and Presence of NO_2. The photo-oxidation mechanism of DTBM initiated by chlorine atoms was investigated in the presence and absence of NO_2. Figure 2 shows the spectra obtained before the photolysis (first trace) and after 70 min of irradiation (second trace). Further spectra correspond to products (third trace) and reference spectra of acetone and formic acid. The subtraction of both reference spectra from the trace of products (paying special attention to the bands at 1775 and 1105 cm^{-1} for $HC(O)OH$, and 1365 and 1217 cm^{-1} for
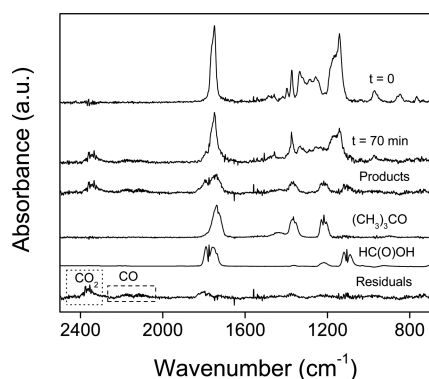
Figure 2. Photo-oxidation of DTBM in the absence of NO$_2$. Traces from top to bottom: before irradiation, after 70 min of photolysis, products, acetone, and formic acid reference spectra, and residuals after subtraction of $(CH_3)_2CO$ and $HC(O)OH$ to "products".

$(CH_3)_2CO)$ leads to the residuals spectrum, from which the signals corresponding to carbon monoxide and carbon dioxide, highlighted by the dashed and the dotted squares, respectively, are easily seen.

Figure 3 shows the set of spectra obtained when the reaction is carried out in the presence of NO$_2$. The sequence starts with
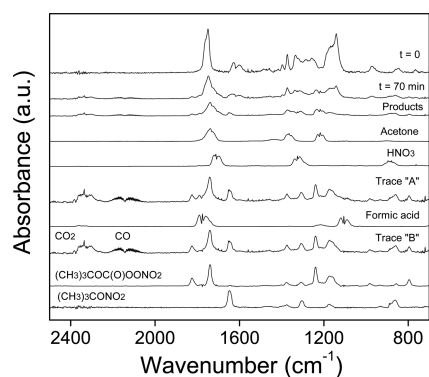

Figure 3. Photo-oxidation of DTBM in the presence of NO$_2$. Traces from top to bottom: before irradiation, after 70 min of photolysis, products, acetone, and nitric acid reference spectra, trace "A" obtained by subtraction of of $(CH_3)_2CO$ and HNO$_3$ to "products", formic acid, trace "B" obtained by subtraction of formic acid to trace "A" where it is clear the formation of carbon dioxide and carbon monoxide, $(CH_3)_3COC(O)OONO_2$ and $(CH_3)_3CONO_2$ reference spectra.

the trace before the lamps are on and follows with the trace after 70 min of irradiation, and their subtraction, that is, total products. Subsequent traces correspond to reference spectra of acetone and nitric acid, and their subtraction from the trace of total products ("Trace A"). Further traces correspond to the reference spectrum of formic acid, the result of its subtraction to "Trace A" (named "Trace B"), and reference spectra of $(CH_3)_3COC(O)OONO_2$ and $(CH_3)_3CONO_2$. The last two reference spectra (peroxynitrate and nitrate) were obtained through synthesis of bulk quantities following photo-oxidation of mixtures of trimethylacetaldehyde, $(CH_3)_3COC(O)H$, initiated by chlorine atoms in the presence of nitrogen dioxide in gas phase using a proven methodology.[10,18]

According to the photo-oxidation products observed in the absence and presence of nitrogen dioxide, the reaction mechanism presented in Scheme 1 was proposed. The scheme

describes only the attack to the methyl group on account of the SAR methods estimation as was discussed.

The photo-oxidation initiated by the abstraction of the H atom is followed by its reaction with oxygen to form the peroxy radical $(CH_3)_3COC(O)CH_2C(O)OC(CH_3)_2CH_2OO^\bullet$, which subsequently reacts with chlorine atoms, other peroxy radicals, or nitrogen monoxide (formed from photolysis of NO$_2$ when it is present), leading to the formation of the alkoxy radical $(CH_3)_3COC(O)CH_2C(O)OC(CH_3)_2CH_2O^\bullet$.

A priori, the possible reactions paths for this radical are similar to those reviewed by Orlando et al.[19] for alkoxy radicals: decomposition, isomerization via 1,5-H shifts, α-ester rearrangement, and reaction with molecular oxygen or nitrogen dioxide (when added to the system).[19] Taking into account its structure, isomerization via 1,5-H shifts is not possible. Furthermore, its structure is similar to the radical formed in the photo-oxidation of $CH_3C(O)OC(CH_3)_3$ studied by Picquet-Varrault et al.,[20] $CH_3C(O)OC(CH_3)_2CH_2O^\bullet$, who concluded that decomposition to form formaldehyde (CH_2O) and the $CH_3C(O)OC(CH_3)_2^\bullet$ radical is the main path, rearrangement being just a minor contribution. The analysis presented by Orlando et al. for similar radicals, $C_xH_{2x+1}OC(CH_3)_2CH_2O^\bullet$ (x = 1, 2) also supports the idea that unimolecular dissociation is the main fate.[19] Thus, taking into account the rate coefficient for dissociation, $(1-2) \times 10^7$ s^{-1}; the rate coefficients for reaction with oxygen and nitrogen dioxide $\sim 10^{-14}$, and $(2.5-3.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively;[19,21,22] the concentration of oxygen and nitrogen dioxide present in our system, 2.5×10^{19} and 5×10^{15} molecules cm^3, respectively; and the reaction rate ratios (decomposition/reaction with oxygen) and (decomposition/reaction with NO$_2$) give values of at least 80 and 130, respectively, leading to the conclusion that only decomposition prevails.

Then, unimolecular decomposition of $(CH_3)_3COC(O)CH_2C(O)OC(CH_3)_2CH_2O^\bullet$ leads to the formation of $(CH_3)_3COC(O)CH_2C(O)OC(CH_3)_2O^\bullet$ radicals (from now on called IO$^\bullet$ radical), that react mainly by two processes: migration of a hydrogen atom from the methylene group to the oxygen radical (path a), and rupture of the C−O bond of the tertiary carbon atom with immediate decarboxylation (path b).

The migration of the hydrogen atom (path a) leads to the formation of the $(CH_3)_3COC(O)C^\bullet HC(O)OC(CH_3)_2OH$ radical (from now on called IC$^\bullet$), which in the presence of O$_2$, RO$_2^\bullet$, chlorine atoms, or NO goes to $(CH_3)_3COC(O)CHO^\bullet C(O)OC(CH_3)_2OH$. This radical also allows the migration of one hydrogen atom, as it was similarly proposed for the $CH_3(CH_2)_5CHO^\bullet(CH_2)_2CH(OH)CH_2CH_3$ radical by Zhang et al.,[23,24] and then the decomposition occurs, yielding acetone, carbon dioxide, and the $(CH_3)_3COC(O)CHO^\bullet(OH)$ radical. On the contrary, the rupture of the IO$^\bullet$ radical (path b) leads through a series of reactions to the formation of acetone and the $(CH_3)_3COC(O)CH_2^\bullet$ radical.

To compare the different energy processes between paths a and b, the software Gaussian09 was used.[9] The geometric parameters for all the reactants, transition states, and products of the studied reactions were fully optimized using density functional theory with the B3LYP functional and the 6-311+G(d,p) basis set.[12]

The reaction path a was calculated using the QST2 method to locate the transition state, considering the (IO$^\bullet$) radical as the reactant and the (IC$^\bullet$) radical as the product. The results showed that the energy necessary to reach the optimal

Scheme 1. Reaction Mechanism for Photo-oxidation of DTBM Initiated by Chlorine Atoms[a]
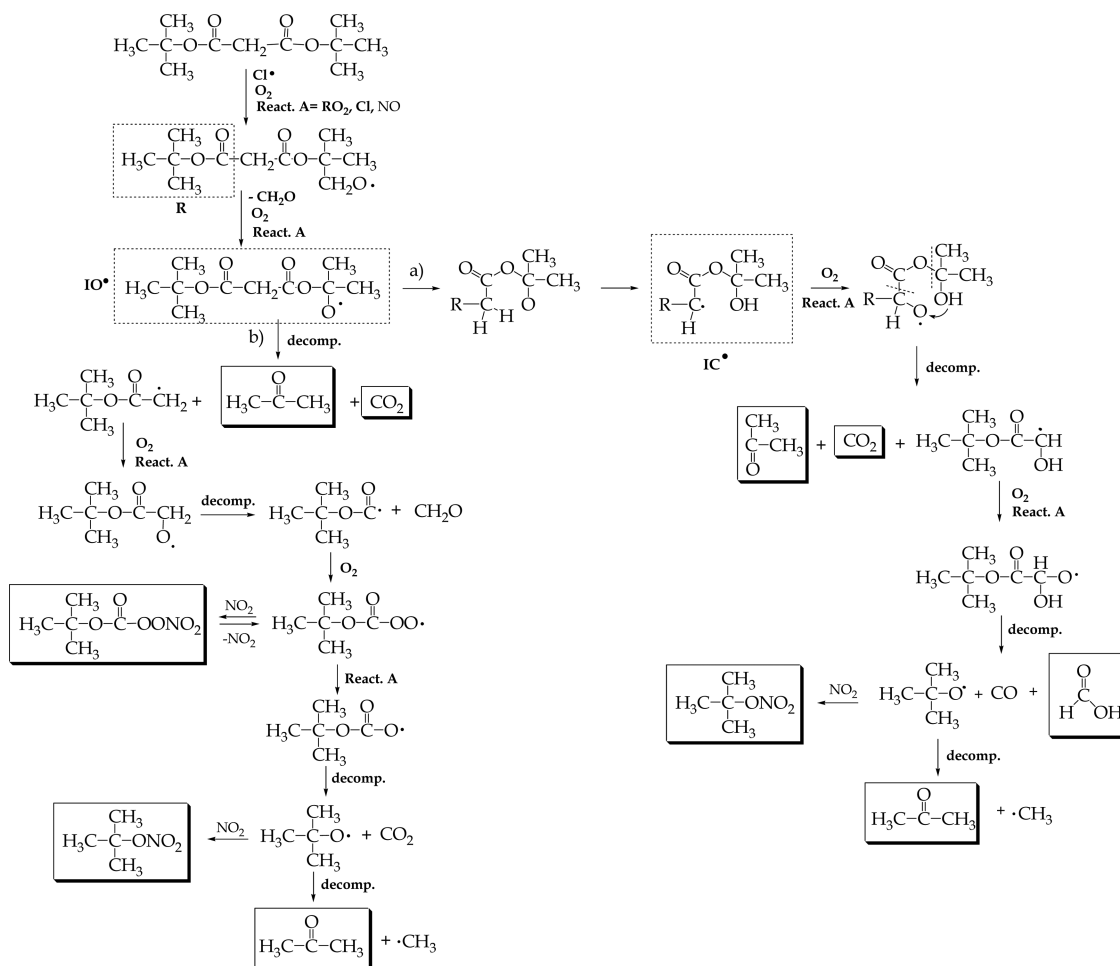
[a]"React. A" represents the reaction of peroxy radicals with chlorine atoms, other peroxy radicals, or nitrogen monoxide.
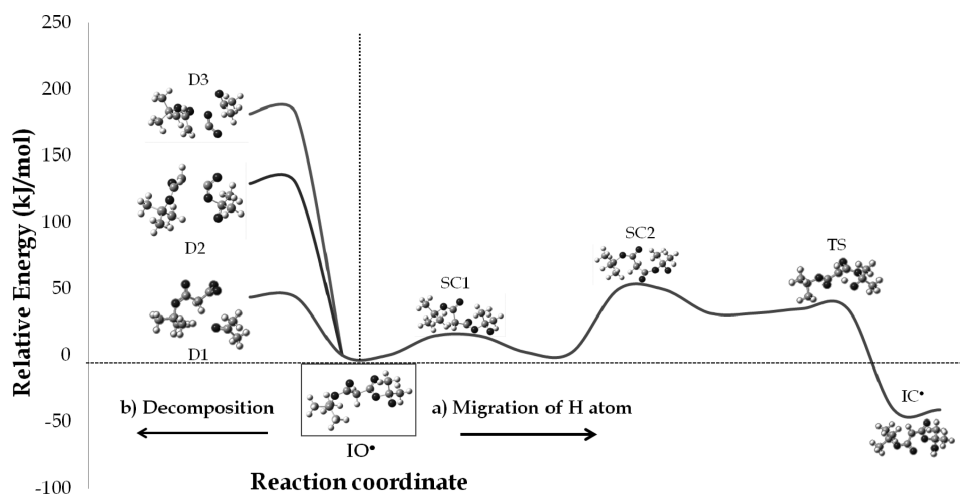

Figure 4. Reaction coordinate for migration of the hydrogen atom (path a) and decomposition (path b) for the IO• radical.

conformation to allow the hydrogen migration is even higher (49.7 kJ/mol) than the energy of the transition state (35.2 kJ/mol) itself. Reaction path b was calculated considering three cases: first, breaking the O–C(O) bond (D1); second, breaking the CH$_3$–C bond (D2); and third, the simultaneous breaking of the former two bonds in a concerted way (D3). The results showed that the least energy path corresponds to D1 (43.9 kJ/

mol). Figure 4 shows the relative energy corresponding to paths a and b. As can be seen, both paths are energetically possible, in accordance with the experimental results.

The decomposition forms (CH$_3$)$_3$COC(O)CH$_2$O• radical, which is the same formed in the study of photo-oxidation of *tert*-butyl acetate performed by Picquet-Varrault et al.[20] Therefore, their conclusions are the same as ours; that is,

unimolecular decomposition is the main fate to form the following oxy radicals with one carbon atom less in the molecule that goes to the formation of the only peroxynitrate observed and continues the decarboxylation until the tertiary oxy radical, $(CH_3)_3CO^\bullet$, is formed. Once this situation is reached, decomposition is no longer the main fate. Instead, reaction with molecular oxygen to form acetone and reaction with nitrogen dioxide to form *tert*-butyl nitrate, $(CH_3)_3CONO_2$ are the only possible routes, corroborating our experimental results.

Finally, the $(CH_3)_3COC(O)CHO^\bullet(OH)$ radical formed from path b decarboxylates to form formic acid, and $(CH_3)_3CO^\bullet$ radicals, from which again we can explain the formation of more *tert*-butyl nitrate and acetone.

The quantification of the experimentally measured reaction products in the absence of nitrogen dioxide (acetone and formic acid as main products) leads respectively to percentages of 190% and 40% with respect to the disappearance of the reactant. This high percentage of acetone comes from the fact that for each molecule of DTBM that disappears, two molecules of acetone are formed, as can be seen from the mechanism proposed. Keeping in mind the mechanism, the quantification of products indicates that $40 \pm 3\%$ of reaction comes from path a and $55 \pm 2\%$ from path b.

Respect to the possible contribution of the attack of chlorine atom to methylene group of DTBM, the SAR method indicates that less than 1% would go by this way. Nevertheless, the products formed through this way would have been the same because the first oxy radical formed $(CH_3)_3OC(O)CHO^\bullet C-(O)O(CH_3)_3$ would break apart forming small (less or equal than four carbon atoms) species only.

CONCLUSIONS

The rate coefficient measured for DTBM with chlorine atoms agrees with that estimated by structure−reactivity relationships methods and is consistent with the values reported in bibliography for other compounds. Additionally, the results of the present investigation have helped to elucidate the mechanism of DTBM in the presence and absence of NO_2. In particular, it was assessed that the main reaction paths of the $(CH_3)_3COC(O)CH_2C(O)OC(CH_3)_2O^\bullet$ radical are the migration of H atom of the methylene group to the terminal oxygen atom and the rupture of C−O bond of the tertiary carbon atom with immediate decarboxylation. The experimental results were corroborated by computational calculations.

AUTHOR INFORMATION

Corresponding Author

*F. E. Malanca. Tel: + 54 (351) 535-3866. E-mail: fmalanca@fcq.unc.edu.ar.

Notes

The authors declare no competing financial interest.

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