Title
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Permalink
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Journal
Journal of physical chemistry, 96(3)

Authors
Schmoltner, A.M.
Anex, D.S.
Lee, Yuan T.

Publication Date
1991-05-01
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A. Schmoltner, D.S. Anex, and Y.T. Lee

May 1991
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IR Multiphoton Dissociation of Anisole: 
Production and Dissociation of Phenoxy Radical

Anne-Marie Schmoltner, Deon S. Anex, and Yuan T. Lee

Department of Chemistry
University of California

and

Chemical Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.
IR MULTIPHOTON DISSOCIATION OF ANISOLE:
PRODUCTION AND DISSOCIATION OF PHENOXY RADICAL

Anne-Marie Schmoltner, Deon S. Anex, and Yuan T. Lee
Chemical Sciences Division,
Lawrence Berkeley Laboratory and
Department of Chemistry, University of California,
Berkeley, California 94720

ABSTRACT

The infrared multiphoton dissociation (IRMPD) of anisole in a molecular beam was studied using pulsed CO₂ laser radiation. The only primary process identified was the dissociation into phenoxy and methyl radicals. Under conditions of higher laser fluence, secondary dissociation of the phenoxy radical into carbon monoxide and C₃H₅ was observed. The product recoil energy distribution was measured using the time-of-flight technique.
Introduction

The infrared multiphoton dissociation (IRMPD) of polyatomic molecules has been established as an excellent experimental technique for studying dissociation mechanisms under isolated conditions. IRMPD of medium sized or large molecules is characterized by fast intramolecular energy distribution after absorption of many IR photons, making it possible to use intense IR radiation to prepare hot ground state molecules similar to those prepared by thermal excitation.\textsuperscript{1-3} Subsequent dissociation processes take place according to the same mechanisms as thermal decomposition.\textsuperscript{3} Since IR multiphoton absorption can take place under collision-free conditions, detailed information about unimolecular decomposition processes of molecules in their electronic ground state can be obtained in experiments using a molecular beam.

The technique used in our laboratory, photofragmentation translational spectroscopy is particularly well suited for the unambiguous identification of primary dissociation products and for the derivation of detailed information on the dissociation dynamics from the measurement of product angular and velocity distributions. Mass spectroscopic
detection makes the method applicable to a vast range of systems.

The thermal decomposition of anisole has been studied repeatedly, and the only primary dissociation channel identified was cleavage of the weak O-CH$_3$ bond to form the methyl radical and the phenoxy radical.

\[
\text{C}_6\text{H}_5\text{-O-CH}_3 \rightarrow \text{C}_6\text{H}_5\text{-O}^\bullet + \text{CH}_3
\]  (1)

At temperatures above 1000K the unimolecular decomposition of the phenoxy radical into carbon monoxide and the cyclopentadienyl radical was observed. Colussi et al. suggested a mechanism for phenoxy radical decomposition involving a bridged \(\text{C}_6\text{H}_5\text{O}\) species (Scheme 1). This mechanism is compatible with the low A-factor and low activation energy for the process obtained by Lin and Lin.

The phenoxy radical is an important intermediate in the combustion of aromatic hydrocarbons. The reaction of oxygen atoms with benzene leads to the production of the phenoxy radical and phenol, and the decomposition of phenol in turn produces phenoxy radicals. The reaction of molecular oxygen with the phenyl radical was postulated as an additional pathway for the production of the phenoxy radical.
One of the goals of our recent investigations has been to find efficient and clean ways of producing phenoxy radicals and to study the dynamics of their decomposition. In our IRMPD experiments, we did find that production of the phenoxy radical was the only primary channel of anisole decomposition at moderate fluence. However, at high laser fluence, the secondary decomposition of some of the phenoxy radicals was observed.

Experimental

The apparatus used in this experiment has been described in detail previously.\textsuperscript{14} Briefly, a supersonic molecular beam was crossed at 90° with the output of a pulsed CO\textsubscript{2} laser. Time-of-flight (TOF) spectra of the photodissociation products were recorded using a mass spectrometer detector consisting of an electron-impact ionizer, quadrupole mass filter, and Daly ion counter. Rotation of the differentially pumped molecular beam source around the axis defined by the laser beam allowed the angle between molecular beam and detector to be varied.

A continuous supersonic beam of anisole was formed by bubbling helium or nitrogen through anisole held at
20°C. The gas mixture at a total pressure of 100-150 Torr was passed through heated lines into the beam source. The nozzle had an aperture of 125 μm diameter and was held at 150°C or 200°C in order to prevent the formation of molecular clusters in the expansion. Typical beam velocities for He-seeded beams were 1.45-1.65x10⁵ cm/s, with speed ratios of about 8-10. The beam velocity distributions were measured using the time-of-flight method.

Two different pulsed CO₂ lasers were used. The earlier experiments were performed using a Gentec DD-250-B TEA CO₂ laser, the later ones using a Lumonics TEA-820 CO₂ laser. The laser radiation was focused using a 25 cm focal length ZnSe lens. The spot sizes were estimated from burning patterns on tape and paper. With the Gentec Laser, fluences were estimated to be 8-17 J/cm² with laser spot sizes of approximately 1 mm², with the Lumonics Laser fluences of up to 27 J/cm² over about 4 mm².

The best yield was observed at the P(26) line of the 001-020 band at 1041 cm⁻¹. The fundamental frequency of the O-CH₃ stretch was determined¹⁵ to lie at 1039 cm⁻¹ and is most likely responsible for the initial absorption at this wavelength.

For a given laboratory angle, TOF spectra were recorded for each laser shot. The signal was
accumulated in a multichannel scaler triggered by the laser pulse. Dwell times of 1-5 μs/channel were used. The data acquisition and storage was handled by an LSI-11 laboratory computer.

Anisole was obtained from Matheson and was degassed in several freeze-pump-thaw cycles. A GC-MS analysis revealed a minor impurity of benzoic acid (about 0.3%). This impurity was found not to interfere in our experiments, as its vapor pressure is considerably lower than that of anisole.

Results and Analysis

Even though the product molecules or radicals fragment extensively upon ionization in the mass spectrometer, parent-daughter ion relationships can be established by identifying common features in the TOF spectra for different mass-to-charge ratios (m/e). Corresponding fragment pairs can be identified using the condition of momentum conservation in the center-of-mass coordinate system.

TOF spectra were measured at laboratory angles between 6° and 50° at m/e=15, 28, 29, 30, 31, 39, 65, 75, 76, 77 and 93, corresponding to the ions CH₃⁺, CO⁺, CHO⁺, CH₂O⁺, CH₃O⁺, C₂H₅⁺, C₂H₅⁺, C₆H₅⁺, C₆H₅⁺, C₆H₅⁺, and
\[ C_6H_5O^+. \] The parent ion of the expected product of anisole decomposition, phenoxy radical, has a mass of 93 amu; however, major fragments were found at \( m/e=39 \) and \( 65 \), with \( m/e=39 \) showing the highest count rate. TOF spectra are shown in Figs. 1-5.

Figs. 1 and 2 show data taken in the first set of experiments using the Gentec laser at low fluence (about 15 J/cm\(^2\)), while Figs. 3-5 represent data taken at higher laser fluence (27 J/cm\(^2\)) using the Lumonics CO\(_2\) laser. The spectra of \( m/e=39, 65 \) and 93 at 8° (Figs. 1 and 2) show only one feature which is the same for all three masses except for a small shift due to the flight time of the ions through the quadrupole mass spectrometer, which is a function of the ion \( m/e \). This feature in the TOF spectra can be identified as the phenoxy radical. The corresponding second fragment, methyl radical, was detected at \( m/e=15 \) and the TOF distribution is shown in Fig. 1. TOF spectra of \( m/e=39 \) at three different laboratory angles are shown in Fig. 2.

In contrast to these results, the TOF spectra obtained in the second set of experiments (at higher laser fluence) show an additional feature. The comparison of the spectra at \( m/e=39, 65, \) and 93 (Figs. 3 and 4) reveals the occurrence of two different reaction channels: The slower feature in all three spectra again corresponds to the phenoxy radical, while the faster
feature can be identified with the decomposition product of the phenoxy radical, the cyclopentadienyl radical. Methyl radical was again detected at m/e=15, and the TOF spectra at three different laboratory angles are shown in Fig. 5. Despite the high detector background at m/e=28, we were able to obtain a TOF spectrum at m/e=28 as well (Fig. 3). The detection of very fast CO at m/e=28 corroborates the identification of the fast feature in the m/e=39 and 65 spectra with the secondary dissociation products of phenoxy radical. Fig. 4 shows TOF spectra of m/e=39 at six different laboratory angles, illustrating the relative contributions of the two channels at different angles. At angles of 20 and larger, only secondary product can be observed.

The appearance of the photodissociation products in the laboratory frame is illustrated in the Newton diagram shown in Fig. 6. Short velocity vectors originating at the tip of the beam velocity vector represent the center of mass velocity of the phenoxy radical recoiling from the methyl radical. The kinetic energy corresponding to this velocity is the maximum energy for this channel as determined by the analysis below. The smaller circle in Fig. 6 represents the possible resultant vectors arising from the addition of the molecular beam velocity to the center of mass velocities. The larger arrows and circle represent the
velocity of the cyclopentadienyl radical recoiling from carbon monoxide in the secondary decomposition of the phenoxy radical. Again, the maximum kinetic energy from the data analysis which is discussed below was used to determine the velocity shown. In the complete Newton diagram for the sequential decomposition process, a collection of secondary circles would appear, each corresponding to particular primary velocity. Also shown in this diagram are several source-detector angles. If a resultant velocity vector falls on one of these lines, then that fragment will be detected at this angle. As can be seen from Fig. 6 the primary phenoxy radical will not be seen at laboratory angles of 20 degrees and higher, whereas the secondary cyclopentadienyl radical may be detected beyond 40 degrees.

The data of m/e=65 and 93 in Fig. 3 show slow components (arriving later than approximately 400 μs) that were not accounted for in the data analysis. These slow features did not originate from the photodissociation of anisole in the beam. They were identified as resulting from time-dependent desorption of anisole molecules from laser heating of a cold surface in the vacuum chamber and did not interfere with the analysis of the IRMPD signal.
A forward convolution method was used in the analysis of the data in order to determine the translational energy distribution of the reaction products, $P(E_r)$. From a trial input translational energy distribution, the TOF distributions were calculated and averaged over beam velocities, the finite dimensions of the interaction zone, and the finite size of the ionizer and then compared with the experimental data. The trial $P(E_r)$ was then adjusted and the process repeated until the best fit was obtained. The angular distributions of the products in the center-of-mass frame were found to be isotropic as expected. The solid lines in Figs. 1-5 represent the fits to the data. The $P(E_r)$ distributions for the primary channel under the two different experimental conditions are shown in Fig. 7, and the $P(E_r)$ for the secondary dissociation is shown in Fig. 8.

The translational energy distributions for the primary product phenoxy radical generated at two different laser fluences (Fig. 7) are almost identical. Both distributions peak at 3 kcal/mol and extend to about the same maximum value, 17 and 18 kcal/mol, respectively. The differences are small but real. For the conditions of lower laser fluence, the $P(E_r)$ is slightly narrower and the average recoil energy is 4.4 kcal/mol, while for higher laser fluence the
distribution is somewhat wider and the average recoil energy is about 5.0 kcal/mol.

The recoil energy distributions in both cases are fairly well characterized since different TOF spectra are sensitive to different parts of the P(E_r). The data for the phenoxy radical at larger angles (12-15°) represent the high energy tail of the distribution. The fits of the m/e=15 distributions at small angles, on the other hand, are particularly sensitive to the low energy part of the P(E_r).

It has to be emphasized that in all cases the spectra stemming from methyl radical and those stemming from phenoxy radical could be fit with the same recoil energy distributions. However, the minimum recoil energy required for phenoxy to reach the detector at 6° is 2.2 kcal/mol (for a typical beam velocity), whereas the minimum recoil energy required for methyl to reach the detector at 10° is only 0.2 kcal/mol. Thus it is possible that the P(E_r) distributions for the two fragments deviate at very small recoil energies because of the secondary decomposition of some highly vibrationally excited (and thus slow) phenoxy radicals.

The P(E_r) for the secondary reaction, Fig. 8, shows a threshold value of 8 kcal/mol and a maximum energy release of 48 kcal/mol. These values probably have uncertainties of about 2 kcal/mol.
Discussion

Several conclusions can be drawn from the recoil energy distributions obtained from this experiment. The only primary process, dissociation into phenoxy radical and methyl radical, shows the same characteristics for both conditions studied. The fact that the translational energy released in the formation of phenoxy and methyl radicals at higher laser fluence does not differ substantially from that of lower laser fluence indicates that the high rate of dissociation of vibrationally excited anisole is limiting the further absorption of IR photons. In changing the laser energy fluence by 80 percent the energy level from which the anisole molecules dissociate does not change significantly.

The fact that the translational energy distributions peak at a small but finite value suggests the existence of a barrier in the C₆H₅O-CH₃ dissociation. This is in contrast to simple bond rupture processes which have been demonstrated by previous investigations of IRMPD to result in translational energy distributions that peak at zero energy in accordance with the predictions of statistical theory. A barrier for the bond rupture process considered here could
result from the electronic rearrangement associated with the partial C-O double bond character in the phenoxy radical. This also explains the fact that in the reverse reaction of methyl radicals with phenoxy radicals the methyl prefers to attach to the o- and p- positions of the benzene ring rather than the oxygen atom.\textsuperscript{19}

The phenoxy radicals which were produced in the earlier part of the laser pulse continue to absorb IR photons and dissociate into cyclopentadienyl radicals and carbon monoxide. This secondary process has a large barrier. Lin and Lin\textsuperscript{5} determined that this step has an activation energy of $44.0\pm0.9$ kcal/mol.

The large energy release (up to 48 kcal/mol) and the peaking of the translational energy distribution at 14 kcal/mol in the secondary process is indicative of the substantial barrier for this reaction. The dissociation of phenoxy radical to cyclopentadienyl and carbon monoxide is 20 kcal/mol endothermic.\textsuperscript{9,20}

Consequently, some of the phenoxy radicals must have been excited beyond 68 kcal/mol internal energy. The known thermochemistry of the present system is summarized in Fig. 9.

Our results therefore indicate that the IRMPD of anisole is a possible and convenient way of producing phenoxy radicals. No other primary products were
observed, and with sufficient control of the laser fluence, secondary products could be prevented.

Conclusions

In the IRMPD of anisole the only primary decomposition channel occurring is rupture of the weak $^8,^9$ O-CH$_3$ bond forming phenoxy and methyl radicals. The recoil energy distribution suggests the existence of an exit barrier for this dissociation channel. Under higher laser fluence conditions, the secondary dissociation of the phenoxy radical was observed. The large recoil energy release is in accordance with the existence of a sizable exit barrier for this process as determined by Lin and Lin.$^5$

Acknowledgment

This work was supported by the Director, Office of Energy research, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract DE-AC03-76SF00098.
References

3. Oref, I.; Rabinovitch, B. S. Acc. Chem. Res. 1979, 12, 166.


Figure Captions

Fig. 1  TOF spectra of m/e=93 and m/e=65 at 8° and m/e=15 at 15° obtained at low laser fluence.

Fig. 2  TOF spectra of m/e=39 at 8°, 12°, and 15° obtained at low laser fluence.

Fig. 3  TOF spectra of m/e=93, 65, and 28 at 10° obtained at high laser fluence.

Fig. 4  TOF spectra of m/e=39 at 6°, 10°, 13°, 20°, 30°, and 40° obtained at high laser fluence showing the primary (long dashed curve) and the secondary (short dashed curve) channels.

Fig. 5  TOF spectra of m/e=15 at 10°, 30°, and 50° obtained at high laser fluence.

Fig. 6  Newton or velocity diagram illustrating primary and secondary dissociation channels. The shorter vectors originating at the tip of the beam velocity vector correspond to the primary dissociation product, the phenoxy radical. The longer vectors originating at the tip of a phenoxy radical velocity vector correspond to the secondary dissociation product, the cyclopentadienyl radical. The underlined species indicate which is the detected fragment for each channel. At angles of 20° and larger only secondary products appear.
Fig. 7 Translational energy distributions, $P(E_t)$, for the primary dissociation channel of anisole for low laser fluence (solid curve) and high laser fluence (dashed curve).

Fig. 8 Translational energy distribution, $P(E_t)$, for the secondary dissociation channel of anisole.

Fig. 9 Energy diagram for the primary and secondary dissociation process in the IRMPD of anisole.
Scheme 1.

\[
\begin{align*}
&\text{O}^* \\
&\text{O} \\
&\cdot\text{CO} \\
\downarrow & \quad \text{+} \\
&\text{CO}
\end{align*}
\]
Fig. 1

Counts / 1000 Laser Shots

m/e=93
8°

m/e=65
8°

m/e=15
15°

Flight Time (μs)

XBL 8910-3570
Counts / 1000 Laser Shots

Flight Time (μs)

0 0

m/e = 39
12°

m/e = 39
15°
Fig. 3
Counts / 1000 Laser Shots

Flight Time (μs)

m/e=39
6°

m/e=39
10°

m/e=39
13°

m/e=39
20°

m/e=39
30°

m/e=39
40°

XBL 8910-3568

Fig. 4
Fig. 5

The graph shows the counts per 1000 laser shots as a function of flight time in microseconds for different angles.

- m/e = 15, 10°
- m/e = 15, 30°
- m/e = 15, 50°

The peaks indicate the number of counts at each flight time for each angle.
Fig. 8