

OXIDATION OF SOME VAPOR FREE LIQUID ORGANIC COMPOUNDS BY A LOW PRESSURE OXYGEN PLASMA.

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ABSTRACT

Results from interactions of non equilibrium oxygen plasmas with both gaseous and liquid substrates are presented. High voltage and radio frequency plasmas are generated by electron impact with O_2 molecules which give rise to species such as O , O_2^+ , O^- and, consequently, more electrons which are accelerated by the electric field and keep the discharge on. Oxidation products plus polymeric material are obtained if an 100:1 oxygen-hydrocarbon gas mixture is used. As this ratio tends towards 1:1, fragmentation and condensed products, arising from oxygen free organic radicals, are formed instead. Conversely, O^3P addition to the hydrocarbon is the unique process that takes place if the oxygen plasma is allowed to impinge on the surface of the liquid substrate. Results are optimum when the temperature of this liquid is so low that its vapor pressure is about 0.01 torr. Some theoretical approaches of the processes are discussed.

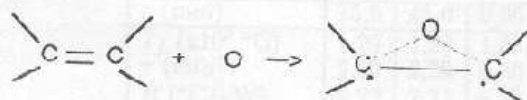
1. Introduction

The oxidation of hydrocarbons in a low pressure oxygen plasma involves atomic oxygen as the principal reacting agent. Oxygen atoms are generated into the discharge and the organic material is either injected as a gas behind the plasma zone or is fed into the reactor together with molecular oxygen.

With saturated compounds atomic oxygen reacts, most likely, by abstraction of hydrogen and formation of radicals (1-3).



With olefins, the formation of an activated three member ring, which could be either stabilized as epoxide or opened up to a hot birradical, seems to be the most probable route of reaction(4).



Under these conditions cyclohexene originates the corresponding oxide and two carbonyl compounds (5); the oxide is also the main product of 2-methyl-propene, but the presence of 2-metoxipropene (traces) has been taken as an evidence of CH_3 group migration (6). Intramolecular migration has been pointed out also with cis, trans 3,4-dimethyl-3-hexene (DMH) and 3-ethyl-2-methyl-2-pentene (EMP). The carbonyl compounds formed are in both cases the same. That is only possible if the C_2H_5 group migration is assumed (6,7).

Furthermore, if the hydrogen abstraction takes place, radicals such as phenyl and OH should be formed. This causes further reactions and the resulting plasma sample is much more complicated to analyze. This last situation is quite common in practically all plasma experiments with organic materials either pure or diluted with a reactive or inert gas (8).

In spite of the new and interesting synthetic possibilities offered by the organic non-equilibrium plasma state reactions, at least four disadvantages should be remarked.

- 1.- Reactions are limited to organic material which can be evaporated without decomposition.
- 2.- Selectivity is very low.
- 3.- Reactants frequently form polymers which accumulate everywhere on the walls and on the electrodes causing difficulties with the cleaning of the apparatus.
- 4.- Depending on the thickness of the film deposited on the electrodes, the discharge characteristics change and the results are no longer reproducible.

More recently the oxidation reactions have been carried out in a different way. The oxygen plasma was formed, far away from the bottom of the reactor where the organic compound is placed and cooled down to a controlled temperature (9-11). Experiments with saturated and unsaturated organic substances have shown that all the above complicated reactions do not occur any more; both, selectivity and yields are improved, polymers formation is quite completely avoided; time of oxidation is also reduced because the reaction is carried out in batch.

In the following sections a short review of the experimental developments and the conditions under which the oxidation is favored is given. An attempt of diagnostic and its significance to preparative organic chemistry is also discussed.

2. Experimental techniques

A plasma can be considered as a new way of transferring

energy to molecules. Since results depend almost exclusively on the electron energies and the temperature of the substrate, the discharge types or the frequencies used are of little importance, the choice of the equipment being mainly based on practical criteria.

The most versatile and simple device as well as typical arrangements largely used for organic chemistry reactions in gaseous phase are discussed elsewhere (12,13). For plasma experiments, where a pure oxygen plasma is formed and allowed to impinge on the vapor free surface of a liquid substrate, the reactors used are a little bit different from those in references 12 and 13. Hence they shall be treated in some details. The power sources have been a radio frequency and a high-voltage glow discharge. Since the results with both techniques are quite similar, the last one has to be preferred for it is simple, easy to handle, home made and fairly cheap.

2.1. Radio frequency (R.F.) discharge

The plasma can be fed by either capacitive or inductive coupling, the last one being the most commonly used for laboratory works in organic synthesis. Since only certain frequency bands are permitted for scientific experiments, generators with a fixed frequency, e.g., 13.4 MHz, and variable power (0-500 watts) are preferred. In addition, to obtain an efficient coupling of the power to the discharge reactors, a matching box is necessary.

The generator we have used is a Branson IPC 100. The glass reactor looks like a trap (Fig.1) with an inlet for O_2 and an output connected to a vacuum line. The organic substance is cooled down at the bottom of the reactor. The plasma oxygen pressure (not higher than 0.5 torr) and the power supplied (less than 100 watt) are experimentally chosen so that a stable oxygen glow is obtained. With the help of the matching box, the glow is confined to the internal tube of the discharge reactor.

2.2. High-voltage (H.V.) glow discharge

In a high-voltage typical arrangement, two metal electrodes are placed into the reactor (14). A rare gas is introduced through the electrodes (15) or in their vicinity, to prevent the contamination by polymeric material that can bridge the gap.

Since all the experiments we are concerned with must be carried out keeping the organic surface free of vapor phase, organic vapors will never reach the electrodes; the formation of polymers on the metallic surface is then completely avoided. The plasma is formed by passing pure oxygen through the electrodes. The glow interacts with the organic substance in a V-shaped glass reactor (Fig.2). Its bottom is easily cooled down by means of a refrigerated bath at a controlled temperature. The organic liquid material is continuously and magnetically stirred.

3. Oxygen plasma-liquid substrate interaction

Two conditions should be fulfilled to assure that atomic

oxygen adds to the liquid organic substrate:

- The liquid should have its vapor pressure as low as possible.
- The atomic oxygen concentration in the gas phase has to be high enough to assure that a representative fraction of it reaches and reacts on the organic surface.

In what follows, some experiments are briefly discussed to illustrate both points.

3.1. Liquid substrate

We have chosen toluene as a model in the discharge for its reactions in gaseous plasmas are well known (16). The products that can be obtained as a result of oxygen addition are easily detected just by comparing the chromatogram of the gaseous plasma sample with that one resulting from O_2 plasma and liquid substrate interaction. Since the vapor phase in equilibrium with the liquid should be as low as possible, to decide on the most convenient working temperature for the oxidation process, a graphic representation of $\log P_v$ (P_v = vapor pressure) against $1/T$ ($^{\circ}K^{-1}$) has been constructed.

All the experimental points of vapor pressure and temperature for various organic materials fit with straight lines (15). This is shown in Fig.3 for toluene. Assuming that this dependence holds even at a very low temperature, the straight lines could be extrapolated (17).

In the oxidation reactions studied by Cvetanovic (1), oxygen reacts more easily when the ratio between the oxygen partial pressure in the discharge and the organic vapor pressure is higher than 50. On this basis, for an oxygen pressure of 1 torr, the organic vapor pressure should be less than 0.02 torr. Assuming that these conditions hold in our case too, the corresponding temperature at which the substrate should be cooled down will be less than $-80^{\circ}C$. At this temperature, toluene is still liquid (melting point $-95^{\circ}C$).

3.2. Atomic oxygen (O^3P)

From spectroscopic constants, the potential energy curves for O_2 and O_2^+ can be constructed. Below 20 eV all the

molecular states, except $b^4\Sigma_g^-$ of O_2^+ , form O^3P at the dissociation (18). The relative concentration of this species is 10^3 higher than others such as O^- and $O(^5S^0, ^5P)$ (19), which disappears mainly through a reaction with a third body. Nevertheless by increasing pressure O^3P forms ozone with O_2 (20).

From the energetic levels of the first oxygen spectrum, it appears that the ground level ($2p^3P$) population can be obtained by measuring the line intensities at 1356 and 1359 Å or at 1302 and 1306 Å which respectively correspond to transitions from $3s^5S^0$ and $3s^3S^0$ to that state. However this is not easy to do because a vacuum spectrograph is needed. the triplet and quintuplet systems through the transitions



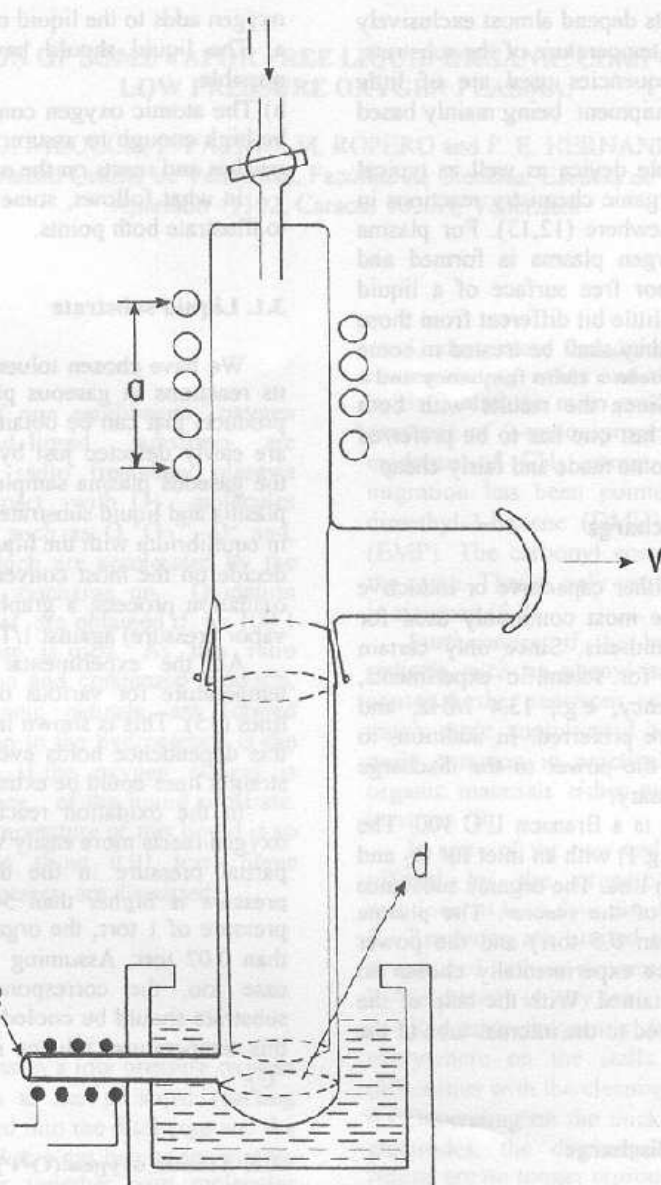


Figure 1 .. R.F. Reactor

j) oxygen inlet; a) R. F. coil; v) vacuum line connection; e) optic window and heater; d) bottom of the reactor where the organic substance is cooled down and magnetically stirred

The wavelengths are 8446, 4368 and 8447 Å for the triplet and Nevertheless the $2p^3P$ population can be correlated to both 7772 and 7775 Å for the quintuplet levels. So a visible spectrograph that is much cheaper than a vacuum one, can be used to monitor the O^3P during the discharge.

Chemically atomic oxygen is effectively captured by mercury oxide (21). A less effective reaction takes place on the reactor glass-wall. In a dark room the presence of O^3P is visualized by means of a pallid yellow color as a consequence of chemiluminescence reactions with nitric oxide. This compound comes out from nitrogen traces which always contaminate commercial oxygen bottles. If the yellow

color is not present at all, it can be thought that the O^3P concentration in the discharge is negligible. Sometimes when O^3P does not exist at all a pale red color, due to the 0,0 band of the atmospheric $^1\Delta_g \rightarrow ^3\Sigma_g^-$ transition. Under these conditions the discharge can be used as a good source of singlet oxygen ($O_2^1\Delta_g$).

Figure 4 shows the emission of O^3P as a function of the pressure in the discharge. At a constant power, the emission increases when the pressure is lowered to a limit where the discharge collapses. At a constant power and pressure the temperature of the reactor has little or no influence on the emission intensity(22).

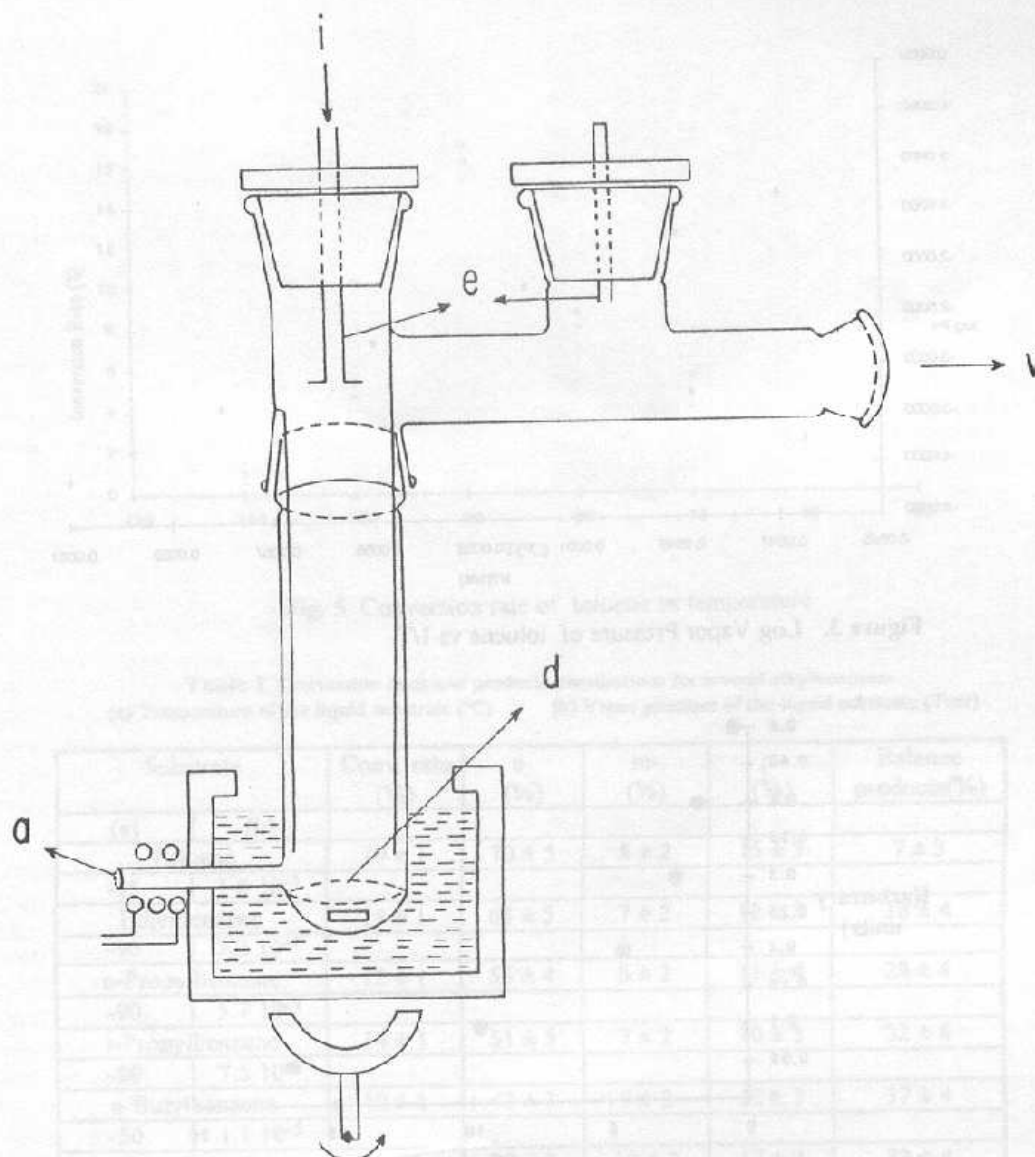


Figure 2 - H.V. Reactor

j) oxygen inlet through the aluminium electrode, e) electrodes are connected to an a.c. or d.c. source; v) vacuum line connection, a) optic window and heater; d) bottom of the H.V. reactor where the organic substance is cooled down and magnetically stirred.

3.3. Experimental results

At a constant power, the oxygen pressure in the discharge was arranged so that a maximum emission was obtained for the line at 4368 Å. A Czerny Turner spectrometer equipped with a plane 1200 lines/mm grating blazed at 5000 Å was used. The signal from an RCA 4302 photomultiplier has been amplified and printed on a chart recorder.

The reactor window (a and e in Fig.1 and 2 respectively) was as close as possible to the liquid surface. For all the experiments, 3 ml of liquid has been used. The temperature of the substrate was maintained at a constant value by means of a thermostat, COLORA Model TK 9R, which is able to control the bath temperature with a deviation of $\pm 1^\circ\text{C}$. The time of reaction was chosen in such a way that the oxidation was not higher than 20 %, so that successive reactions were minimized.

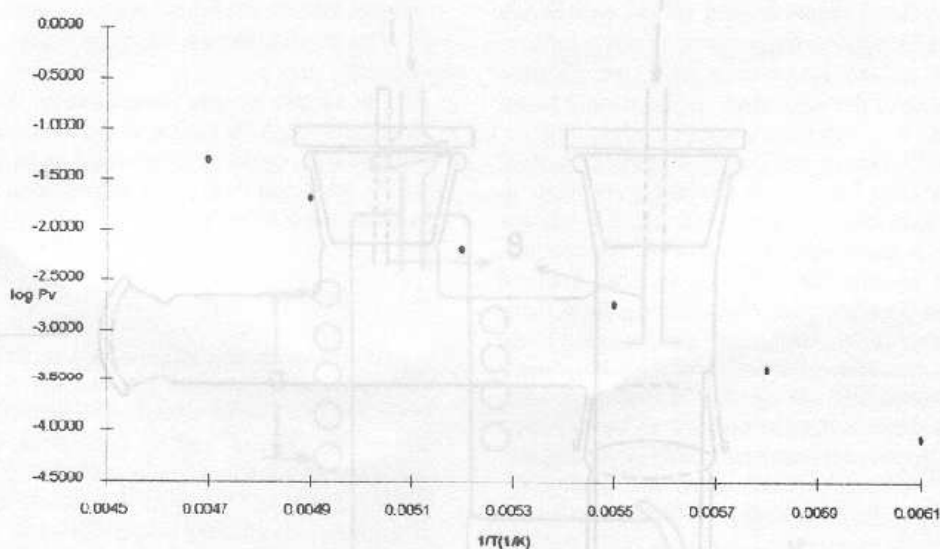


Figure 3. Log Vapor Pressure of toluene vs $1/T$

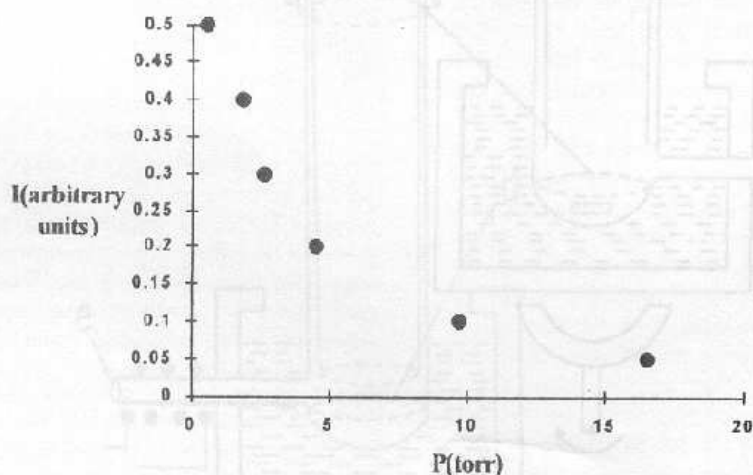


Fig. 4 Emission of O_3P ($\lambda = 4368 \text{ \AA}$) vs O_2 pressure in the discharge.

In Figure 5 oxidation percentage of toluene at different temperatures has been plotted, providing that all other parameters, oxygen flow, vacuum speed of the pump, power of the source, etc., were kept constant. With the help of Figure 3, the vapor pressure of toluene can be calculated for each temperature. Its value (torr) is reported in parenthesis on Figure 5. The maximum oxidation was found near the melting point of toluene ($P_v = 1.8 \times 10^{-3}$ torr). Since the oxygen pressure in the discharge was 0.1 torr, the ratio was very close to that previously reported.

The sample analysis was performed by G.C. using an UCW 982/CROMOSORB W column, 6 feet long and 1/8 inches external diameter.

The major oxidation product (70 %) was o-methylphenol. The two other components, m- and p-methylphenol, represent less than 23 %. The walls of the reactor were clean and no products were found into the traps that connect the reactor to the vacuum pump. These traps are cooled down by a liquid nitrogen bath.

The same plot as in Figure 5, can be drawn out with any other compound. When they are oxidized, results are quite similar to those of toluene (Table I). Methylcyclohexane should be treated as a special case. In spite of the fact that there is not a double bond in the molecule, the oxygen addition takes place on the tertiary carbon and methylcyclohexanol is the only product formed. Provided

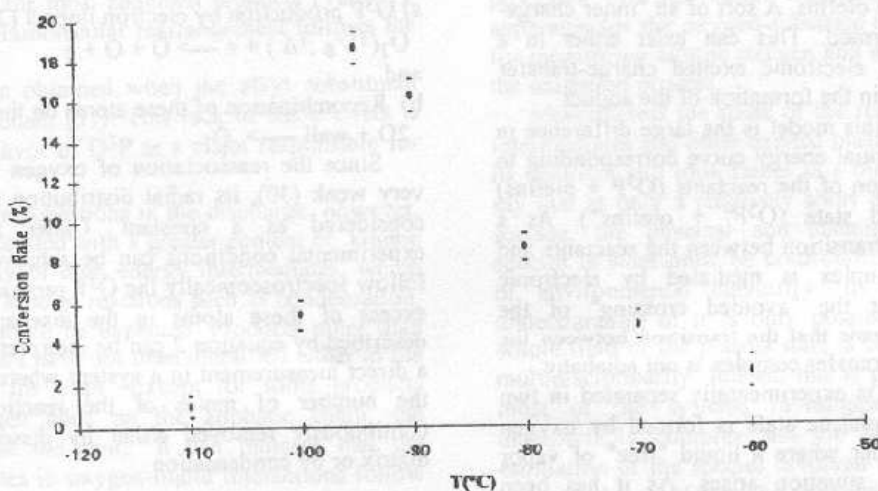


Fig. 5 Conversion rate of toluene vs temperature.

Table I. Conversion rates and products distributions for several alkylbenzenes.
 (a) Temperature of the liquid substrate (°C) (b) Vapor pressure of the liquid substrate (Torr)

Substrate	Conv. rate (%)	o- (%)	m- (%)	p- (%)	Balance products (%)
(a) (b)					
Toluene	19 ± 1	70 ± 5	8 ± 2	15 ± 3	7 ± 3
-95 1.8 10 ⁻³					
Ethylbenzene	14 ± 1	63 ± 5	7 ± 2	12 ± 3	18 ± 4
-90 3.2 10 ⁻⁴					
n-Propylbenzene	12 ± 1	55 ± 4	6 ± 2	11 ± 4	28 ± 4
-90 5.7 10 ⁻⁵					
i-Propylbenzene	14 ± 1	51 ± 5	7 ± 2	10 ± 3	32 ± 4
-80 7.5 10 ⁻⁵					
n-Butylbenzene	10 ± 1	42 ± 3	9 ± 2	12 ± 3	37 ± 4
-50 1.1 10 ⁻⁵					
t-Butylbenzene	7 ± 1	38 ± 3	12 ± 2	17 ± 3	33 ± 4
-45 2.8 10 ⁻⁵					

that the experimental conditions are suitable, the oxidation percentages are of the same order or better than those found with aromatic compounds. These results have opened the way to oxidize saturated compounds via an oxygen plasma (22).

When a relatively long aliphatic chain is present as a substituent on the aromatic ring, the main product still corresponds to the addition of O³P at the ortho position, although a little oxidation of the aliphatic chain is also obtained (less than 10 %). These results however are a little bit different from those reported very recently for the oxidation of a group of sixteen olefins, most of them specially synthesized for plasma purpose. Here, the oxygen addition takes place only on the double bond and, depending on its position in the chain, epoxide, aldehyde and ketone are identified (23).

4. Discussion of results

Many attempts have been made to explain the reactions that occur in a low pressure plasma (14). For a given system where reactants, intermediates and products are all in gaseous phase, the rate constants exhibit a non-Arrhenius behavior (24). The most suitable model to explain these results has been mainly based upon the transition state theory (25). Since there will be many possible nuclei configurations with minimum potential energy through which or near which the plasma system would be expected to pass in going from reactants to products, the postulation of multiple reaction channels for these reactions has been advanced (26). More recently (27) a non adiabatic electronic tunneling model has been specifically proposed for the reactions between O³P and olefins. The mechanism takes advantage from the

"electrophilic" character of the O^3P atoms and the electron-donating properties of the olefins. A sort of an "inner charge-transfer complex" is formed. This can exist either in a ground-state or in other electronic excited charge-transfer state, which are involved in the formation of the adduct.

The main feature of this model is the large difference in energy between the potential energy curve corresponding to the ground-state interaction of the reactants (O^3P + olefins) and that of the excited state (O^3P^- + olefins $^+$). As a consequence of this, the transition between the reactants and the charge transfer complex is mediated by electronic tunneling transition near the "avoided crossing" of the potential curves. This means that the transition between the reactants and the charge-transfer complex is not adiabatic.

If the plasma system is experimentally separated in two regions, one where the plasma state is formed by oxygen species only, and the other where a liquid "free" of vapor molecules exists a new situation arises. As it has been pointed out before, all the products identified under these circumstances contain oxygen, which indicates that the main process and probably the only one is the oxidation of the organic material.

Let us, for an instant, adopt the olefin as a model for the oxidation of the substrates we are working with.

1) O^3P + olefins \longleftrightarrow Charge-transfer complex (CTC).

2) CTC \longrightarrow products.

O^3P is formed in the discharge and it is allowed to impinge on the surface. Once there, it interacts with an organic molecule and forms the CTC, the fate of which is determined now by two possibilities:

a) To go back to O^3P and olefin.

b) To stabilize forming oxidation products.

The absence of products without oxygen in the liquid sample, as well as polymeric material on the wall of the reactor or in the liquid substrate, is a good evidence that, if the decomposition of the CTC through the route (a) is allowed, the olefin is not reactive. Furthermore the O^3P released can react with other olefin molecules and by diffusion through the liquid medium can form a less energetic CTC or just O_2 by combination with a second O^3P (23).

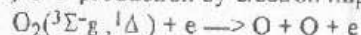
The energy of the CTC depends on the kinetic energy of the O^3P atoms. In a moderate discharge, as is the case in our experiments, the possibility of a high energy intermediate is very remote. Thus the probability of the complex dissociation and the diffusion of O^3P into the liquid until it reacts with another liquid molecule, seems to be very low.

4.1. The oxygen plasma model

It is now evident that a knowledge of the oxygen plasma glow is fundamental to understand the oxidation of "vapor free" liquid organic compounds. On the basis of 23 reactions, coupled to a Boltzmann code, which considers 13 more processes, a kinetic model of the low pressure ($0.1 < P < 5$ torr) oxygen positive column has been recently developed (28). This model predicts, with a good accuracy, the concentration of O^3P and other species such as O (1S), O (1D), O^- , O_2 ($^1\Delta_g$), etc.

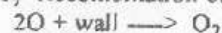
For our purpose two processes should be considered:

a) O^3P production by electron impact (29)



and

b) Recombination of these atoms on the wall of the reactor.



Since the reassociation of oxygen atoms on the wall is very weak (30), its radial distribution in the plasma can be considered as a constant. Under these circumstances, experimental conditions can be achieved, which permits to follow spectroscopically the O^3P production and to create an excess of these atoms in the discharge. The mechanism described by equation 2 can be interpreted now, as a way for a direct measurement in a system where there is a change in the number of moles of the reaction products that is continuously removed either by dissolution in the liquid matrix or by condensation.

4.2. Oxidation of the substrate

The other aspect of the oxidation process is the reaction of O^3P on the liquid surface. Since the working temperature (Fig.3) corresponds to the lowest vapor pressure before the substrate solidifies, the assumption that the reactions mainly involve O^3P atoms and liquid organic molecules seems to be a good approximation.

Furthermore, when the discharge reaches the substrate, products such as biphenyl, bibenzyl and polymers, which are easily formed with substrates as toluene and ethylbenzene, should be expected. These products are not identified in our experiments, in spite of the fact that the glow comes into contact with the surface of the substrate and moves around following the magnetic stirring of the sample. At this point, it should be pointed out that substances such as mesitylene have been easily oxidized if they are mixed with a suitable solvent such as decaline. The unique product identified has been 2-hydroxy-1,3,5-trimethylbenzene (31). This represents another possibility to study the oxidation of a large number of solid substrates that form stable solutions at conditions which favor the oxygen plasma attack.

Nevertheless the possibility of oxidation reactions on the surface like that occurring in gaseous phases, followed by a stabilization of intermediates into the liquid, cannot be definitively ruled out.

Much more information is needed on the rate and mechanisms of the reactions to arrive at a conclusion about the reaction path way and the most probable intermediate that could be formed therein.

Until now experimental results are in good agreement with calculations (32). When the attack of O^3P is on an aromatic ring, the ortho position is favored (Table I), which means that there the ortho electronic density is more appropriated than that corresponding to para position to "catch" the very electrophilic O^3P .

If the formation of a hot birradical is supposed to take place, ortho- and meta-methylphenol should be equally probable. Since the ratio ortho/meta is about 8, there is a possibility that an intermediate different from a hot birradical

should be formed. For all the experiments reported the orthoalkylphenols are the most abundant products (Table I), it indicates that an intramolecular rearrangement follows the intermediate.

Similar results are obtained when the alkyl substituent has a relatively long chain (31). This lack of steric effect is another argument in favor of O³P as a major responsible for the oxidation process.

Under more severe conditions in the discharge, however, O³P atoms can be generated with a greater content of kinetic energy. Thus a variety of high energy intermediates, which could suffer different kind of reactions such as condensation, fragmentation, etc. should be expected. Products other than o-, m- and p-substituent have not been identified either in the liquid sample or in the traps. Except for some products (traces) where oxygen adds on the aliphatic chain, the situation stays almost the same. It can indicate that the energetic intermediates in oxygen-liquid interactions follow routes different from those in gaseous reactions.

On the basis of a non adiabatic electrophilic tunneling model (NETM), which holds in gaseous phase, an inner charge-transfer complex is supposed to be formed near the "avoided crossing" of two possible potential energy curves, one corresponding to ground state reaction and the other to excited state and the reaction is mediated by electronic tunneling transition. If it is assumed that the excited state complexes once formed are able to transfer oxygen atoms to other molecules inside the liquid, a situation can be produced where the possibilities of reaction by direct collision and diffusion of oxygen atoms in the liquid matrix are possible as well. A way to gain more knowledge on that process may be to determine the bimolecular rate constant for the reaction. According to reference (27), the equation for the bimolecular constant has the form:

$$k_{bi} = (\pi\mu)^{-\frac{1}{2}} \left(\frac{2}{kT} \right)^{\frac{1}{2}} \int_0^\infty \sigma(E) \exp\left(-\frac{E}{kT}\right) dE$$

where μ is the reduced mass of the reactants, E is the energy for a particular trajectory defined by a relative collision energy and impact parameter, $\sigma(E)$ is the reaction cross section that should be calculated from the integrated reaction probabilities summed over all the impact parameters.

5. Conclusions

The scope of this short review on the oxidation of a vapor free liquid organic compounds has been primarily for people who are probably more interested in new ways of synthesizing organic oxidized compounds than in the theoretical aspects and physical theories of gaseous discharges and the "plasma state". This is particularly true at this moment when a great deal of interest is centered on reactions in combustion chemistry, atmospheric chemistry and photochemical air pollution. More specifically, in Maracaibo, Venezuela, there is a natural combination of an electric discharge, which arises along the Catatumbo river in

Zulia state, with combustion, photochemical and plasma processes. For this reason, emphasis has been placed on the apparatus for the oxygen-substrate interactions and methods for monitoring atomic oxygen and analyzing the products of the oxidation process.

Nevertheless the route of the reactions, the formation of intermediates and other excited plasma species, its nature and its behavior still look rather as a black box. It is worthily to say that at only a relatively short distance above the earth's surface, the physical and chemical behavior of plasma species is what must be considered to explain some aspects of environmental chemistry. It appears that a fruitful understanding of it is only possible if the research in the whole field of the plasma state is carried out on the basis of multidisciplinary. Indeed, this is partly due to the fact that most of the systems investigated have proved to be unexpectedly complex and the detection and quantitative estimation of the species involved are often very difficult to be carried out. Hence the interpretation of the processes is not necessary correct.

However the possibility of placing new and powerful tools as well as a great number of experimental results in the hands of the modeling workers, represents a good opportunity to pursue solutions and to indicate where we go from here in the field of low pressure plasma chemistry.

6. Acknowledgments

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