Olefinic Ozonation Electron Transfer Mechanism†

Xian-Man Zhang*

Chemistry Department, Wesleyan University, Middletown, Connecticut 06459

Qinyan Zhu

Uniroyal Chemical Company, Inc., World Headquarters, Benson Road, Middlebury, Connecticut 06749

Received February 18, 1997⊗

Ozonations of ammonia, amines, anilines, and *p*-phenylenediamines have been shown to proceed via an electron transfer reaction mechanism. The ozonation rate constants for the alkenes with different substituents were shown to be linearly correlated with the ionization potentials of the corresponding olefinic substrates. The rate constants for the ozonations of methyl-substituted benzenes were also shown to be linearly correlated with the ionization potentials of the corresponding aromatic substrates. These results together with other related experimental evidences lead us to suggest that the olefinic ozonations proceed via an electron transfer reaction mechanism (Scheme 4). This mechanism explains why the derivatives of *p*-phenylenediamine can be used as efficient antiozonants to prevent the degradation of rubber products caused by ozone.

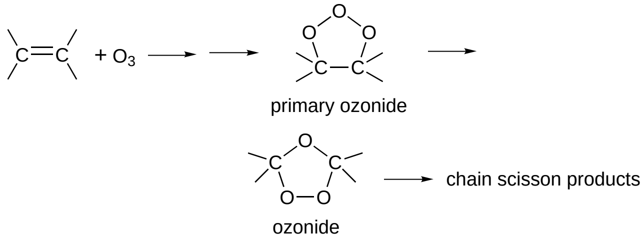
Introduction

Ozone is an allotrope of ordinary atmospheric oxygen in which the molecule is composed of three oxygen atoms rather than two and is one of the most powerful known oxidizing agents. It can react with almost all organic compounds.[1] Reaction of ozone with olefins has been the subject of intensive study for over 100 years.[1,2] The ground-level ozone concentration in normal air is in the range of 1−5 parts per hundred million (pphm), which has been shown to be sufficient to cause elastomer polymer cracking and to destroy the usefulness of rubber products.[3] Reaction of ozone with the double bond of a polymer molecular backbone was believed to be responsible for the fast degradation of rubber (elastomer) products when exposed to the atmospheric air.[4] Prevention of the ozone degradation to increase their service lifetime is known to be the most economical way to reduce the manufacturing cost of the rubber products.

Ozonation is also known as one of the most important and useful reactions used to selectively cleave the olefinic double bond to synthesize ketone and/or aldehyde in synthetic organic chemistry. Ozone has been used for olefinic cleavage oxidation more often than the other oxidizing agents such as permanganate because the ozonation yields are generally much higher and the reactions are much cleaner, gentler, and more versatile.

The olefinic ozonation was generally believed to proceed via a very reactive primary ozonide intermediate formed by a concerted 1,3-dipolar cycloaddition of ozone with the carbon−carbon double bond, which is followed by the rapid ring cleavage and recombination of the primary ozonide to form the ozonide intermediate. Many stable ozonides have been isolated and characterized by ordinary chemical methods.[5] The reduction or hydrolysis of the ozonide intermediates formed gives the final chain scission products (ketones and/or aldehydes dependent on the substitution on the double bond). This is generally called the Criegee ozonation mechanism as depicted in Scheme 1.[6]

Scheme 1



The major drawback of the Criegee olefinic ozonation mechanism (Scheme 1) is not consistent with the prevailing experimental evidences documented in the literature about the existence of radical intermediates from various olefinic ozonations (*vide infra*). In the present paper, we will first discuss the electron transfer reaction mechanism for the ozonations of ammonia, amines, anilines, and *p*-phenylenediamines. Then, we will present the experimental evidences to suggest that the olefinic ozonations also proceed via the electron transfer reaction mechanism (Scheme 4).

Results and Discussion

Ozonations of Ammonia and Aliphatic Amines. Ammonium nitrate has been shown to be the final product for the ozonation of liquid or solid ammonia.[7] The

---

* Author to whom correspondence should be addressed. Phone: 860-685-2210.

† This paper is dedicated to Professor You-Cheng Liu of the Modern Chemistry Department, University of Science and Technology of China.

⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1997.

(1) Bailey, P. S. *Ozonation in Organic Chemistry*, Vol. II; Academic Press: New York, 1982.

(2) Bailey, P. S. *Ozonation in Organic Chemistry*, Vol. I; Academic Press: New York, 1978; Chapter III.

(3) Lattimer, R. P; Rhee, C. K.; Layer, R. W. In *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 3, 4th ed.; Kroschwitz, J. I., Ed.; Wiley: New York, 1992; p 448.

(4) Razumovskii, S. D.; Zaikov, G. E. In *Developments in Polymer Stabilization-6*; Scott, G., Ed.; Applied Science Publication: London, 1983; Chapter 6.

(5) (a) Criegee, R.; Korber, H. *Adv. Chem. Ser.* **1972**. *No. 112*, Chapter 3. (b) Briner, E.; Rossetti, G. P.; Fliszar, S. *Helv. Chim. Acta* **1965**, *48*, 1076.

(6) (a) Criegee, R. *Angew. Chem., Int. Engl. Ed.* **1975**, *14*, 745−752. (b) Kuczkowski, R. L. *Acc. Chem. Res.* **1983**, *16*, 42−47.

(7) (a) Solomon, I. J.; Kacmarek, A. J.; McDonough, J. M.; Hattori, K. *J. Am. Chem. Soc.* **1960**, *82*, 5640. (b) Herman, K.; Giguere, P. A. *Can. J. Chem.* **1965**, *43*, 1746. (c) Solomon, I. J.; Hattori, K.; Kacmarek, A. J.; Platz, G. M.; Klein, M. J. *J. Am. Chem. Soc.* **1962**, *84*, 34. (d) Lucchese, R. R.; Haber, K.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1976**, *98*, 7617.

S0022-3263(97)00297-1 CCC: $14.00

Scheme 2

$$NH_3 + O_3 \rightleftharpoons NH_3{\bullet}O_3 \rightleftharpoons \overset{\bullet+}{N}H_3 + O_3^{\bullet-}$$

first step of the reaction was suggested to proceed via an electron transfer mechanism as shown in Scheme 2 because of the observation of a red-colored salt at lower temperatures, which was assigned as a radical cation salt.[7]

The ozonations of aliphatic amines were also believed to proceed via the electron transfer mechanism since the pink-colored charge-transfer complex intermediates have been observed at the low temperature ozonations of *tert*-butylamine and di-*tert*-butylamine.[8] The most conclusive evidences for the formation of the charge-transfer complexes are the observation of their ESR spectra at the low temperatures.[8]

Ozonations of Anilines and *p*-Phenylenediamines. Ozonations of aniline and its derivatives have been found to produce *p*-benzoquinone, azobenzene, and polymeric products.[9] The formation of these products was attributed to the formation of the aniline radical cation intermediates by an electron transfer mechanism.[9] The polyanilines (conducting polymers) are known to be readily produced by single electron oxidation of anilines via aniline radical cation intermediates.[10]

The initial ozone attack should occur at the nitrogen atom since it has lone pair electrons, which is consistent with numerous experimental observations.[11] For example, no ozonation of amines has been found in formic acid solution because of the protonation of the amine group.[12] When ozone passes through a solution of *p*-substituted-*N*,*N*-dimethylaniline in 70% perchloric acid, no ozonation reaction takes place. But ozone was quantitatively absorbed when the perchloric acid solution was diluted to about 20−25%.[13] The quantitative ozonation of *p*-substituted-*N*,*N*-dimethylaniline is clear due to the formation of the yellow color of free *p*-substituted-*N*,*N*-dimethylaniline in 20−25% perchloric acid solution. The yellow *p*-substituted-*N*,*N*-dimethylaniline is colorless in 70% perchloric acid solution because of the complete formation of the protonated *p*-substituted-*N*,*N*-dimethylaniline.[13]

p-Phenylenediamine and its derivatives are much easier than anilines to be oxidized to form the corresponding radical cation intermediates.[14] For example, *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine can readily be oxidized by various one-electron oxidants to generate a deeply colored stable radical cation, called Wurster's salt.[15] The formation of Wurster's salts from the ozonation of *p*-phenylenediamines provides the convincing evidences for the electron transfer mechanism.[4,15,16] The extremely high reactivities of *p*-phenylenediamines against the one-electron oxidation could be attributed primarily to the high degree of the resonance stabilization of the corresponding radical cation as shown in Scheme 3.

Scheme 3

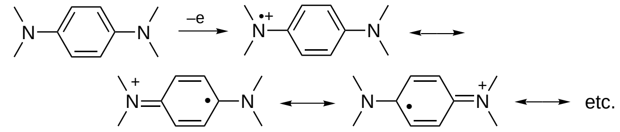


Table 1. Ionization Potentials in the Gas Phase and Oxidation Potentials in DMSO Solution for Some Representative Nitrogen Compounds

nitrogen substrate	ionization potentials (eV)[a]	E_{ox}(HA)[c]
aniline	7.44	0.445[d]
p-methylaniline	7.24	0.305[d]
m-chloroaniline	8.09	0.635[d]
o-chloroaniline	8.5	0.625[d]
p-chloroaniline	8.18	0.535[d]
p-nitroaniline	8.34	0.895[d]
N-methylaniline	7.33	0.446[d]
carbazole	7.57	0.755[d]
diphenylamine	7.16	0.455[d]
o-phenylenediamine	7.29[b]	−0.142
m-phenylenediamine	7.26[b]	−0.04
p-phenylenediamine	6.52[b]	−0.320
N,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine	5.97[b]	

[a] In eV; taken from Lide, D. R. *CRC Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, **1995−1996**; p 10-210 (unless otherwise indicated). [b] Layer, R. W. In *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 2, 4th ed.; Kroschwitz, J. I., Ed.; Wiley: New York, 1992; pp 473−482. [c] In volts; oxidation potentials measured in DMSO solution by cyclic voltammetry and referenced to the ferrocene/ferrocenium couple; this work unless otherwise indicated. [d] Data taken from Bordwell, F. G.; Zhang, X.-M.; Cheng, J.-P. *J. Org. Chem.* **1993**, *58*, 6410.

The high reactivities of *p*-phenylenediamines are also clearly associated with their lower ionization potentials in the gas phase[17a] (or their lower oxidation potentials in solution[17b]). Ionization potentials and oxidation potentials have generally been considered to provide the best quantitative measure about the thermodynamic stabilities of the radical cations formed.[18] The ionization potentials and oxidation potentials for some representative nitrogen compounds are summarized in Table 1. Examination of Table 1 shows that both ionization potentials and oxidation potentials of *p*-phenylenediamines are much lower than those of anilines and other related nitrogen compounds. The data in Table 1 also show that the ionization and oxidation potentials have a good linear relationship.

Electron Transfer Mechanism for Olefinic Ozonations. Although the primary ozonide intermediates are extremely unstable even at very low temperatures, the solution and solid matrix spectroscopic information is known for some primary ozonides.[19] The structure of ethylene primary ozonide has been determined by the

---

(8) (a) Bailey, P. S.; Keller, J. E. *J. Org. Chem.* **1968**, *33*, 2680. (b) Bailey, P. S.; Keller, J. E.; Carter, J. P., Jr. *J. Org. Chem.* **1970**, *35*, 2777.

(9) (a) Reference 1, pp 186−187. (b) Keinan, E.; Mazur, Y. *J. Org. Chem.* **1977**, *42*, 844.

(10) (a) Wei, Y.; Focke, W. W.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. *J. Phys. Chem.* **1989**, *93*, 495−499. (b) Wei, Y.; Sun, Y.; Tang, X. *J. Phys. Chem.* **1989**, *93*, 4878−4881 and references cited therein.

(11) Bailey, P. S. *Chem. Rev.* **1958**, *58*, 925.

(12) Corrodi, H.; Hardegger, E. *Helv. Chim. Acta* **1955**, *38*, 2038.

(13) Kolsaker, P.; Teige, B. *Adv. Chem. Ser.* **1972**, *112*, Chapter 8.

(14) (a) Bacon, J.; Adams, R. N. *J. Am. Chem. Soc.* **1968**, *90*, 6596. (b) Adams, R. N. *Acc. Chem. Res.* **1969**, *2*, 175.

(15) Michaelis, L.; Schubert, M. P.; Granik, S. *J. Am. Chem. Soc.* **1939**, *61*, 1981.

(16) Layer, R. W. *Rubber Chem. Technol.* **1966**, *39*, 1585.

(17) (a) Ionization potential is the potential to remove one electron from a molecule in the gas phase. (b) Oxidation potential is the potential to remove one electron from a molecule in solution.

(18) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55−190.

(19) (a) Hisatsune, I. C.; Shinoda, K.; Heicklen, J. *J. Am. Chem. Soc.* **1979**, *101*, 2524. (b) Kohlmiller, C. K.; Andrews, L. *J. Am. Chem. Soc.* **1981**, *103*, 2578. (c) McGarrity, J. F.; Prodolliet, J. *J. Org. Chem.* **1984**, *49*, 4465. (d) Hull, L. A.; Hisatsune, I. C.; Heicklen, J. *J. Am. Chem. Soc.* **1972**, *94*, 4856. (e) Mile, B.; Morris, G. W.; Alcock, W. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1644. (f) Hisatsune, I. C.; Kolopajlo, L. H.; Heicklen, J. *J. Am. Chem. Soc.* **1977**, *99*, 3704. (g) Nelander, B.; Lord, L. *J. Am. Chem. Soc.* **1979**, *101*, 3769.

millimeter spectra in the gas phase[20] and confirmed by the theoretical calculations.[21] The charge-transfer complexes have been suggested to be formed in the low-temperature ozonations of mesitylene, 1-mesityl-1-phenylethylene, and 1-methoxy-1,2,2-trimesitylethylene.[22] An initial electron transfer from the double bond of the olefinic substrates to ozone has been proposed to explain the formation of the radical intermediates observed at −78 °C for these ozonations as the primary ozonide.[22]

The electron transfer mechanism is consistent with the numerous experimental evidences documented in the literature.[1,2,23] A new visible absorption peak of the charge transfer complex intermediate could always be observed when ozone was mixed with olefinic substrate at low temperatures.[24] The wavelengths of the visible absorption spectra for the aromatic ozonations have been shown to gradually increase as the number of the alkyl substitutions of the double bond increases. This could be attributed to the electron-donating properties of the alkyl substituents, which can stabilize the radical cation intermediates formed and shift the absorption to the red side.[22b]

A strong ESR signal had been observed when unsaturated polymeric rubber was exposed to ozone.[25] Careful experiments have been performed to show that the radical intermediate formed does not come from a second reaction course since the radical intermediate concentration is proportional to the concentration of ozone and the number of the double bonds ruptured.[26] Therefore, we conclude that *the charge-transfer complex should be formed before the primary ozonide formation*. It is also conceivable that the primary ozonide is the charge-transfer complex rather than the 1,3-dipolar addition product.

It is impossible that the radical intermediates observed at the olefinic ozonations were generated from the direct hydrogen atom abstraction from the allylic hydrogen atom by a neutral ozone molecule[23a] even though the theoretical calculations have shown that the ground state of the ozone molecule has a diradical character.[27] Nangia and Benson have estimated that the O−H bond dissociation energy of the $HO_3^{\bullet}$ radical is about 69 kcal/mol,[28] which is consistent with our 66.3 kcal/mol[29] from the theoretical calculations by the CBS-4 model.[30] The allylic and benzylic C−H bonds are the weakest C−H bonds in most unsaturated hydrocarbons, and their bond dissociation energies are known to be in the range of 80−90 kcal/mol.[31] For example, the bond dissociation energy of the allylic C−H bond in propene is 86 kcal/mol, and the benzylic C−H bond is 88 kcal/mol in toluene and 82 kcal/mol in diphenylmethane.[31] In other words, the direct hydrogen atom abstraction by ozone molecule from these allylic or benzylic C−H bonds will be thermodynamically unfavorable by about 15−25 kcal/mol.

Conversely, the hydrogen atom abstraction from the olefinic radical cations by a neutral ozone molecule or an ozone radical anion[32] should be thermodynamically favorable because the reactivities of radical ions are much higher than those of their neutral substrates.[33,34] The bond dissociation energies of the benzylic C−H bonds in toluene and diphenylmethane radical cations were estimated to be 48 and 32 kcal/mol, respectively.[33a] This indicates that the formation of the toluene and diphenylmethane radical cations by removal of one electron weakens the corresponding benzylic C−H bonds by about 40−50 kcal/mol. The hydrogen atom abstraction from the benzylic C−H bonds of the toluene or diphenylmethane radical cations by neutral ozone molecule or ozone radical anion should be thermodynamically favorable (spontaneous).

Correlation of Rate Constants with Ionization Potentials. If the first step of the olefinic ozonation is single electron transfer reaction, it is anticipated that the rate constants for the olefinic ozonations should be related to the ionization potentials of the corresponding olefinic substrates since the olefinic radical cation stabilities will be determined by their ionization potentials.[18]

Wei and Cvetanvic[35] have determined the ozonation rate constants for various substituted olefinic compounds in the gas phase. The relative rate constants, together with the corresponding ionization potentials of the olefinic substrates, are summarized in Table 2. Examination of Table 2 reveals that the rate constants increase as the number of alkyl substituents adjacent to the double bond increases. Interestingly, the relative rate constants have a remarkable correspondence with the ionization potentials of the olefinic substrates. A plot of the logarithm of the ozonation rate constants versus the ionization potentials of the corresponding olefinic substrates is linear with a regression coefficient of 0.96 as shown in Figure 1.

The nice linear correlation indicates that the activation energies of these ozonations are proportional to the ionization potential differences of the corresponding substrates.[36] This also suggests that the electron transfer reaction is the rate-determining step for the ozonations.[37] This explains why the ozonation rate constants for

---

[20] Gillies, J. Z.; Gillies, C. W.; Suvenram, R. D.; Lovas, F. L. *J. Am. Chem. Soc.* **1988**, *110*, 7991.

[21] Mckee, M. L.; Rohlfing, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 2497.

[22] (a) Bailey, P. S.; Ward, J. W.; Potts, F. E.; Chang, Y.; Hornish, R. E. *J. Am. Chem. Soc.* **1974**, *96*, 7228. (b) Bailey, P. S.; Ward, J. W.; Carter, T. P., Jr.; Nieh, E.; Fisher, C. M.; Khashab, A. Y. *J. Am. Chem. Soc.* **1974**, *96*, 6136. (c) Bailey, P. S.; Ward, J. W.; Hornish, R. E.; Potts, F. E., III. *Adv, Chem. Ser.* **1972**, *No. 112*, Chapter 1.

[23] (a) Pryor, W. A.; Prier, D. G.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 2883−2888. (b) Murray, R. W.; Morgan, M. M. *J. Org. Chem.* **1991**, *56*, 684. (c) Murray, R. W.; Ramachandran, V. *J. Org. Chem.***1983**, *48*, 813−816. (d) Bailey, P. S.; Hwang, P. S.; Chiang, C.-Y. *J. Org. Chem.* **1985**, *50*, 231−234. (e) Bailey, P. S.; Southwick, L. M.; Carter, T. P., Jr. *J. Org. Chem.* **1978**, *43*, 2657−2664. (f) Gall, B. L.; Dorfman, L. M. *J. Am. Chem. Soc.* **1969**, *91*, 2199.

[24] Bailey P. S.; Ward, J. W.; Hornish, R. E. *J. Am. Chem. Soc.***1971**, *93*, 3552.

[25] Devries, K. L.; Simonson, E. R. *Ozone Chemistry and Technology*. A Review of the Literature 1961−1974, Franklin Institute Press: Philadelphia, p 257.

[26] Andrews, E. H. *Fracture in Polymers*; Elsevier: New York, 1968.

[27] (a) Dewar, M. J. S.; Olivella, S.; Rzepa, H. S. *Chem. Phys. Lett.* **1977**, *47*, 80. (b) Lee, T. J.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 7062. (c) Stanton, J. F.; Lipscomb, W. N.; Magers, D. H.; Bartlett, R. J. *J. Chem. Phys.* **1989**, *90*, 1077.

[28] Nangia, G. A.; Benson, S. W. *J. Am. Chem. Soc.* **1980**, *102*, 3105−3115.

[29] Zhang, X.-M.; Petersson, G. A. Unpublished results.

[30] Ochterski, J. W.; Petersson, G. A.; Wiberg, K. B. *J. Am. Chem. Soc.* **1995**, *117*, 11299.

[31] McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

[32] Kellersohn, T.; Korber, N.; Jansen, M. *J. Am. Chem. Soc.* **1993**, *115*, 11254.

[33] (a) Zhang, X.-M.; Bordwell, F. G. *J. Org. Chem.* **1992**, *57*, 4163−4168. (b) Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1992**, *114*, 9787−9792. (c) Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1994**, *116*, 904−908. (d) Zhang, X.-M. *J. Chem. Soc., Perkin Trans. 2* **1993**, 2275. (e) Zhang, X.-M.; Bordwell, F. G. *J. Org. Chem.* **1994**, *59*, 2809.

[34] Chanon, M.; Rajzmann, M.; Chanon, F. *Tetrahedron* **1990**, *46*, 6193−6299.

[35] Wei, Y. K.; Cvetanovic, R. J. *Can J. Chem.* **1963**, *41*, 913.

[36] Isaacs, N. *Physical Organic Chemistry*, 2nd ed.; Longman: Essex, England, 1995; Chapter 2.

[37] Wadt, W. R.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1975**, *97*, 3004.

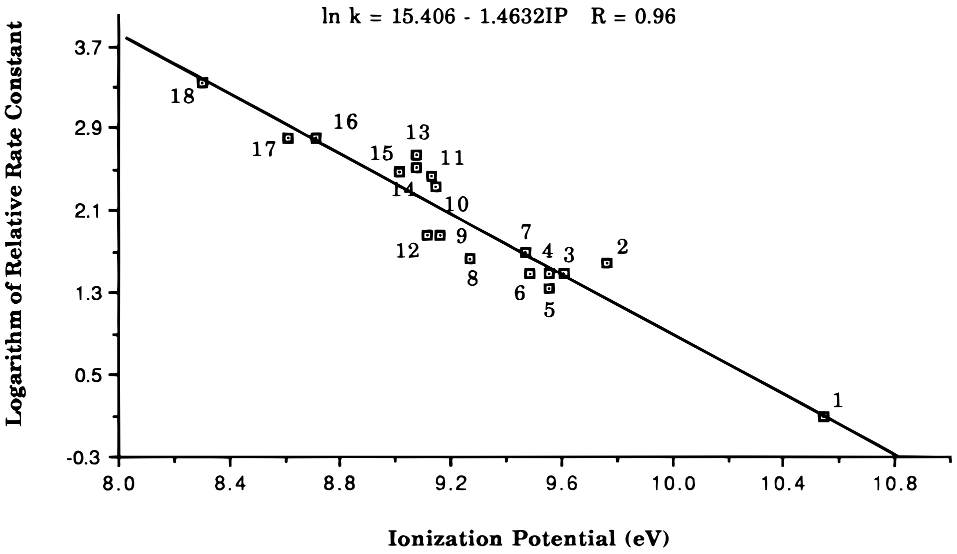


Figure 1. Linear correlation of the logarithm of the ozonation rate constants versus the ionization potentials: (1) ethylene; (2) propene; (3) 1-butene; (4) 1-pentene; (5) 3-methyl-1-butene; (6) 4-methyl-1-pentene; (7) 1-hexene; (8) isobutene; (9) 2-methyl-1-butene; (10) *cis*-2-butene; (11) *trans*-2-butene; (12) 2-methyl-1-pentene; (13) *cis*-2-pentent; (14) *trans*-2-pentene; (15) 4-methyl-2-pentene; (16) 2-methyl-2-butene; (17) 2-methyl-2-pentene; (18) 2,3-dimethyl-2-butene.

Table 2. Relative Ozonation Rate Constants for Substituted Olefins

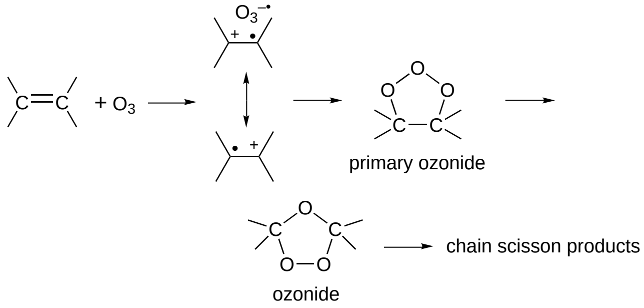
olefinic substrate	ionization potential (eV)[a]	k (L mol^{-1} s^{-1})[b]
ethylene	10.51	1.00
propene	9.73	4.52
1-butene	9.58	4.05
1-pentene	9.52	4.05
3-methyl-1-butene	9.52	3.57
4-methyl-1-pentene	9.45	4.05
1-hexene	9.44	5.00
isobutene	9.24	4.76
2-methyl-1-butene	9.13	5.95
cis-2-butene	9.11	9.52
trans-2-butene	9.10	10.5
2-methyl-1-pentene	9.08	5.95
cis-2-pentene	9.04	11.4
trans-2-pentene	9.04	12.9
4-methyl-2-pentene	8.98	11.0
2-methyl-2-butene	8.68	15.2
2-methyl-2-pentene	8.58	15.2
2,3-dimethyl-2-butene	8.27	26.2

[a] Ionization potentials in the gas phase at 25 °C. Data taken from Lide, D. R. *CRC Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, 1995−1996; p *10*-210. [b] Relative gas phas ozonation rate constants under a nitrogen atmosphere.[36]

halogenated olefins are much slower than those for the related non-halogenated olefins. The ozonation rate constants were found to dramatically decrease as the number of chlorine substituents increases because chlorine has a much larger electronegativity than does carbon.[38] The electron density of the carbon−carbon double bond will decrease as the number of the chlorine substituents increases.

The linear correlation of Figure 1 also suggests that the ozonation of nonsubstituted ethylene proceeds via the electron transfer mechanism even though no charge-transfer complex has been observed in the condensed phase at low temperature.[19d] It is, however, consistent with the observation of the ozone ethylene complex in the gas phase.[39] Therefore, we believe that the Criegee ozonation mechanism needs to be modified by addition of the electron transfer reaction in order to interpret the experimental observations. The new mechanism is shown in Scheme 4.

Scheme 4



The formation of radical cation intermediates is consistent with the negative ρ (∼−1.0) values for the ozonation of a series of olefins containing aromatic substituents.[40] The electron transfer mechanism is also consistent with the antiozonant protection mechanism for the elastomer (rubber) products.[41] Antioxidants[42] and antiozonants[41] play a very important role in the polymer industry. From a chemical point of view, the ozonation mechanism for the small alkenes should be same as that for the unsaturated polymer molecules. The olefinic radical cation intermediates formed from the ozonations (Scheme 4) should be readily quenched by *p*-phenylenediamine since the ionization potentials of *p*-phenylenediamine and its derivatives (Table 1)[43] are about 2 eV

---

(38) Williamson, D. G.; Cvetanovic, R. J. *J. Am. Chem. Soc.* **1968**, *90*, 4248.

(39) (a) Gillies, C. W.; Gillies, J. Z.; Suenram, R. D.; Lovas, F. J.; Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **1991**, *113*, 2412. (b) Gillies, J. Z.; Gillies, C. W.; Suenram, R. D.; Lovas, F. L.; Stahl, W. *J. Am. Chem. Soc.* **1989**, *111*, 3073.

(40) (a) Whitworth, A. J.; Ayoub, R.; Rousseau, Y.: Fliszar, S. *J. Am. Chem. Soc.* **1969**, *91*, 7128. (b) Henry, H.; Zador, M.; Fliszar, S. *Can. J. Chem.* **1973**, *51*, 3398.

(41) (a) Zhang, X.-M. *Recent Research Development in Organic Chemistry*; Transworld Research Network, Vol. II, in press. (b) Zhu, Q, Chen, Z.; Zhang, X.-M. *Polym. Degrad. Stab.* In press.

(42) Zhu, Q.; Zhang, X.-M.; Fry, A. J. *Polym. Degrad. Stab.* **1997**, *57*, 43−50.

(43) Layer, R. W. In *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol 2, 4th ed.; Kroschwitz, J. I., Ed.; Wiley: New York, 1992; pp 473−482.

Table 3. Relative Ozonation Rate Constants for the Methyl-Substituted Benzenes

aromatic substrate	ionization potential (eV)[a]	*k* (L mol^{-1} s^{-1})[b]
benzene	9.246	1.00
toluene	8.82	5.9
o-xylene	8.56	29.3
m-xylene	8.56	27.9
p-xylene	8.44	33.9
mesitylene	8.41	150
durene	8.04	382
pentamethylbenzene	7.92	1786
hexamethylbenzene	7.85	8750

[a] In eV; ionization potentials in the gas phase at 25 °C. Data taken from Lide, D. R. *CRC Handbook of Chemistry and Physics*, 76th ed.; CRC Press: Boca Raton, 1995−1996; p *10*-210. [b] Relative rate constants measured in carbon tetrachloride.[46]

(46 kcal/mol) lower than those of 2,3-dimethyl-2-butene, the lowest ionization potential in Table 2. It is not unexpected that most of the efficient antiozonants on the market are the derivatives of *p*-phenylenediamine.[44] The tremendous differences in ionization potential are consistent with the fact that addition of a small amount (less than 5%) of antiozonants can efficiently prevent the rubber products from the ozone degradation until all of the antiozonants are exhausted.[45]

The ozonation rate constants for a series of methyl-substituted benzenes in carbon tetrachloride are summarized in Table 3,[46] along with the ionization potentials of the corresponding aromatic compounds. The ozonation rate constants for aromatic compounds are expected to be much smaller than those for olefinic compounds because of the much larger activation energies necessary to destroy the aromatic resonance structure in the formation of the corresponding radical cations.[47] Nevertheless, the ozonation rate constants dramatically increase as the number of the methyl substituents increases.[48] The logarithm of the ozonation rate constants can also be linearly correlated with the ionization potentials of the corresponding aromatic substrates with a regression of 0.97 as shown in Figure 2. The good correlation also suggests that the aromatic ozonations proceed via the electron transfer mechanism (Scheme 4).

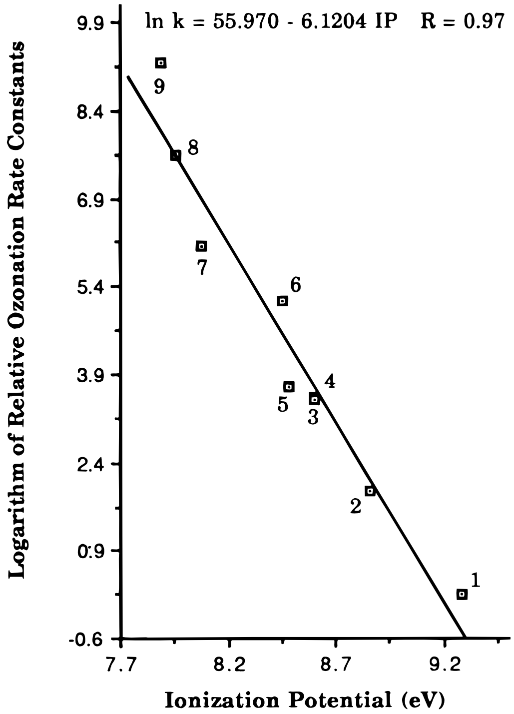


Figure 2. Linear plot of the logarithm of the relative ozonation rate constants versus the ionization potentials: (1) benzene; (2) toluene; (3) *o*-xylene; (4) *m*-xylene; (5) *p*-xylene; (6) mesitylene; (7) durene; (8) pentamethylbenzene; (9) hexamethylbenzene.

Experimental Section

The oxidation potentials of the nitrogen compounds were measured by conventional cyclic voltammetry similar to the method described previously.[49] The working electrode consisted of a 1.5 mm diameter platinum disc embedded in a cobalt glass seal. It was polished with 0.05 μm Fisher polishing aluminum or cleaned with an ultrasonic instrument, rinsed with ethanol, and dried before each run. The counter electrode was platinum wire (BAS). The reference is Ag/Ag$^+$ couple, but the reported oxidation potentials are all referenced to the ferrocene/ferrocenium couple.

Acknowledgment. We are grateful to Mr. Douglas A. Pippin and Mr. Jerome C. Shiels for their proofreading of the manuscript.

JO970297S

---

(44) Berrand, G.; Leleu, E. *Rubber World* **1985** *192*, 32−35.

(45) (a) Cox, W. L. *Rubber Chem. Technol.* **1959**, *32*, 364. (b) Erickson, E. R.; Berntsen, R. A.; Hill, E. L.; Kusy, P. *Rubber Chem. Technol.* **1959**, *32*, 1062. (c) Razumovskii, S. D.; Batashova, L. S. *Rubber Chem. Technol.* **1970**, *43*, 1340.

(46) Nakagawa, T. W.; Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1960**, *82*, 269.

(47) Razumovskii, S. D.; Zaikov, G. E. *J. Org. Chem. USSR (Engl. Transl.)* **1972**, *8*, 473.

(48) (a) Sixma, F. L. J.; Boer, H.; Wibaut, J. P. *Recl. Trav. Chim. Pays-Bas* **1951**, *70*, 1005. (b) Bernatek, E.; Karlsen, E.; Ledael, T. *Acta Chem. Scand.* **1967**. *21*, 1229.

(49) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 9790−9795.