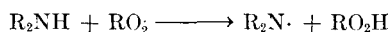
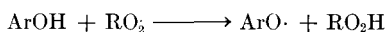


Deuterium Isotope Effect in Inhibited Oxidation of Butadiene-Styrene Rubber

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INTRODUCTION

Various hypotheses have been presented to explain the mechanism of antioxidant action. The generally accepted (but not established) mechanism in the case of aromatic amines and phenols involves the removal of a labile hydrogen by a peroxy radical as a controlling step of the reaction.¹



If hydrogen abstraction is a controlling step in chain termination, it is reasonable to expect that substitution of a labile hydrogen by deuterium should give rise to a kinetic isotope effect. The rate of chain termination should be decreased by deuterium substitution, thereby lowering the antioxidant efficiency and increasing the rate of oxidation of the substrate.

The existence of a kinetic isotope effect in some oxidation reactions and related steps have been previously established. Westheimer and Nicolaides² have reported an isotope effect in the chromic acid oxidation of 2-deuterio-2-propanol. Likewise Max and Deatherage³ have observed a normal isotope effect in the autoxidation of 8,8,11,11-tetradeuterio-cis-9-octadecene. In the reaction of acyl peroxides with phenols when O—H was replaced by O—D, several peroxide-phenol-solvent systems showed a small but constant isotope effect, indicating that O—H cleavage is a rate-controlling step in the reaction.⁴

Kinetic studies by Bickel and Kooyman^{5,6} on both amine and phenolic antioxidants support the theory of hydrogen abstraction as a controlling step. Kuzminskii^{7,8} in correlating antioxidant efficiency with structure reached the conclusion that those groups which activated the labile hydrogen or stabilized the resulting radical increased the antioxidant efficiency. Kinetic studies in this laboratory⁹ of inhibited oxidation of rubber were consistent with a mechanism based on donation of hydrogen to RO_2 by the antioxidant.

However, literature reports have also demonstrated a failure to observe an isotope effect with aromatic amine antioxidants. Hammond, Boozer, and co-workers^{1,10} have reported no effect upon the rate of oxidation when

they compared diphenylamine with *N*-deuteriodiphenylamine, and *N*-methylaniline with *N*-deuterio-*N*-methylaniline, in the oxidation of cumene and tetralin. Pedersen¹¹ has reported no difference in the effect of *N,N'*-diphenyl-*p*-phenylenediamine and *N,N'*-dideuterio-*N,N'*-diphenyl-*p*-phenylenediamine on the induction period of gasoline oxidation.

These authors, because of their failure to find an isotope effect, have concluded that hydrogen abstraction is not the controlling step. They propose instead that either π -complex formation with the peroxy radical,¹⁰ or electron abstraction by the peroxy radical,¹¹ is the rate-controlling reaction.

The present investigation was undertaken in an attempt to clarify the mechanism of antioxidant action by comparing the effects of normal and deuterated antioxidants in the oxidation of synthetic rubber polymer. *N*-phenyl-2-naphthylamine and 2,6-di-*tert*-butyl-4-methylphenol were used in this study.

EXPERIMENTAL

Using a modification of the Zerewitinoff active hydrogen analysis,¹² *N*-phenyl-2-naphthylamine (Eastman Kodak Co.) was reacted with methylmagnesium iodide in anhydrous ethyl ether. The resulting Grignard compound was reacted with 99.5% deuterium oxide. The product, *N*-deuterio-*N*-phenyl-2-naphthylamine, was recovered by vacuum evaporation and fractional crystallization from the ether solution. The highest deuterium content was obtained with product I (uncorrected melting point 107.0–107.7°C.) which was at least 60% substituted with deuterium, while product II (uncorrected melting point 107.5–108.5°C.) corresponded to at least 46% deuterium substitution. Normal *N*-phenyl-2-naphthylamine, to be used for comparison, was reacted in the same manner but was hydrolyzed with H₂O.

2,6-Di-*tert*-butyl-4-methylphenol (Shell Chemical Co.), also containing an active hydrogen, was treated in exactly the same manner as described above for the amine. The deuterated product (uncorrected melting point 68.0–69.0°C.) corresponded to at least 77% of the theoretical deuterium substitution.

Analyses for deuterium substitution were made by reacting portions of the substituted antioxidants with more methylmagnesium iodide. The evolving gas, which was a mixture of methane and deuteriomethane, was collected, and the ratio of the two determined in a mass spectrometer. This gives a minimum value for the substitution since any water contamination in the solvent or from the atmosphere would lead to high yields of methane.

The butadiene–styrene polymer (GR-S 1000) was coagulated by NaCl–H₂SO₄ from a completely uninhibited latex which was specially prepared in stainless steel equipment and stored under nitrogen until used.

The volumetric oxygen absorption technique, described in previous publications from this laboratory,^{13,14} was used to measure the rate of oxygen uptake by the polymer. The procedure previously employed with vulcanizates was modified for use with polymers by pressing the sample onto aluminum screen to give adequate support and uniformity of thickness at elevated temperatures. Sample thicknesses were between 0.030 and 0.050 in., below the thickness required to limit the oxidation rate by diffusion of oxygen at 90°C.

RESULTS AND DISCUSSION

The oxygen absorption curves, obtained at 90°C. and one atmosphere oxygen pressure for the oxidation of butadiene-styrene polymer containing three parts per hundred of the normal and deuterated hindered phenol, are shown in Figure 1 based on the data of Table I. A kinetic isotope effect was exhibited for the 2,6-di-*tert*-butyl-4-methylphenol. Utilizing only the constant rate portions of the curves beyond 300 hours at 90°C., a k_D/k_H ratio of approximately 1.3 was obtained with a deuterium substitution of not less than 77% in the phenol.

The same antioxidant in a concentration of only one part per hundred showed no significant difference in oxidation rate for the normal and deuterated phenol. This was attributed to the fact that the isotope differences were small at this concentration and that the autocatalytic stage of uninhibited oxidation was reached before any significant differences in rate could be established.

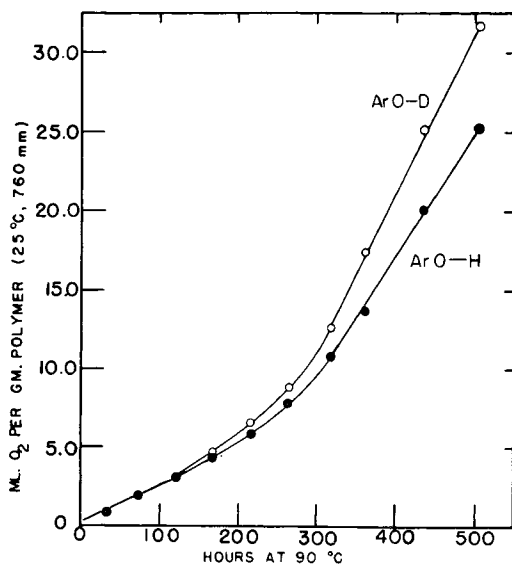


Fig. 1. Kinetic isotope effect in the oxidation of butadiene-styrene polymer inhibited by normal and deuterated 2,6-Di-*tert*-butyl-4-methylphenol, 90°C., 1 atm. oxygen pressure.

TABLE I
Oxygen Absorption Data for the Oxidation of Butadiene-Styrene Polymer Inhibited by
Normal and Deuterated 2,6-Di-*tert*-butyl-4-methylphenol, 90°C., 1 Atm. O₂
Antioxidant Concentration: 3 Parts per Hundred

Hours at 90°C.	Ml. O ₂ per gram polymer (25°C., 760 mm.)	
	Normal phenol	Deuterated phenol
5.5	0.2	0.3
22.75	0.8	0.9
46.5	1.4	1.6
71.0	2.0	2.2
94.5	2.5	2.8
165.75	4.4	4.9
214.25	6.0	6.6
262.25	7.8	8.9
315.0	10.9	12.6
358.25	13.7	17.5
406.5	17.9	22.7
457.5	22.0	27.4
502.0	25.3	31.7

The appearance of an isotope effect with the phenolic inhibitor is reasonable since other workers^{2,6,15-17} have presented evidence that hydrogen abstraction from the O—H group is an important step in the attack of peroxy and other radicals on alkylated phenols.

However, the mechanism of amine antioxidant action is not so well established and seems to be much more complex. The oxygen absorption data (at 90°C. and 1 atm. oxygen pressure) for the oxidation of butadiene-styrene polymers containing normal and deuterium-substituted *N*-phenyl-2-naphthylamine (PBNA) at a concentration of 3 parts per hundred are

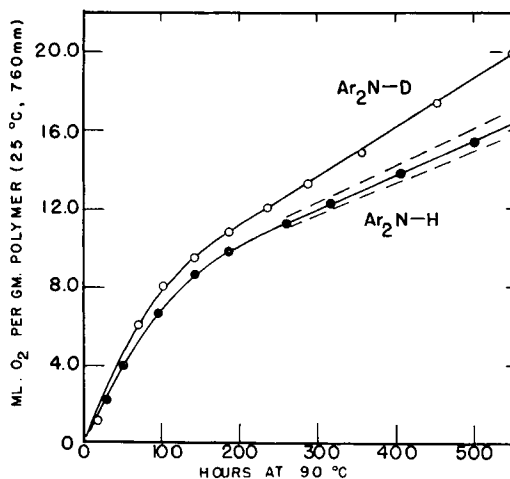


Fig. 2. Kinetic isotope effect in the oxidation of butadiene-styrene polymer inhibited by normal and deuterated *N*-phenyl-2-naphthyl-amine, 90°C., 1 atm. oxygen pressure.

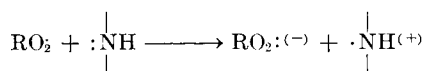
presented in Table II. The kinetic isotope effect observed gives a k_D/k_H ratio of 1.8 ± 0.3 in the constant rate portion of the curve in Figure 2 with a deuterium substitution of not less than 60%. The dashed lines adjacent to the curve for $\text{Ar}_2\text{N}-\text{H}$ represent the standard deviation of the data and emphasize the fact that the two curves are significantly different. A second polymer sample containing the same concentration of PBNA with only 46% deuterium substitution exhibited an isotope ratio of 1.3.

TABLE II

Oxygen Absorption Data with Standard Deviations for the Oxidation of Butadiene-Styrene Polymer Inhibited by Normal and Deuterated *N*-Phenyl-2-naphthylamine, 90°C., 1 Atm. O_2
Antioxidant Concentration: 3 Parts per Hundred

Ml. O_2 per gram polymer (25°C., 760 mm.)				
Hours at 90°C.	Normal amine	Std. dev.	Deuterated amine	Std. dev.
3.75	0.17	0.02	0.19	0.03
19.5	1.2	0.03	1.4	0.05
42.0	3.1	0.10	3.6	0.07
70.0	5.4	0.17	6.1	0.07
103.5	7.3	0.19	8.1	0.04
142.5	8.7	0.18	9.5	0.17
211.5	10.4	0.20	11.4	0.03
287.5	11.8	0.37	13.3	0.04
356.0	13.0	0.36	14.9	0.02
451.0	14.6	0.49	17.4	0.09
546.5	16.2	0.62	19.9	0.16
621.75	17.7	0.74	22.2	0.26

Pedersen¹¹ interpreted his findings on antioxidant efficiencies in gasoline to suggest that the chain termination reaction could result by electron abstraction from the amino groups:



Boozer and Hammond,^{1,10} as a result of their work including the effect of deuterated amines in the autoxidation of cumene and tetralin, concluded that chain termination of an RO_2 radical resulted, not from hydrogen abstraction, but rather by formation of a π -complex involving the antioxidant and RO_2 which is then decomposed by reaction with another RO_2 radical.

However, Bickel and Kooyman⁶ have taken exception to the work of Boozer and Hammond on the basis that the absence of an isotope effect is inconclusive if the activation energy is unknown. They have made rough calculations in one case to show that the activation energy of the $\text{AH}-\text{RO}_2$ reaction studied was close to zero, leading to a prediction of a very small isotope effect. Following the reasoning that a less active attacking radical

might give a larger isotope effect, since the activation energy would be higher, Bickel and Kooyman observed an isotope ratio of 1.95 between diphenylpicrylhydrazyl and the normal and deuterated 2,6-di-*tert*-butyl-4-methylphenol in toluene at 20° to 30°C.

The results of the present study as reported above show an isotope effect in the inhibited oxidation of rubber, using both amine and phenolic antioxidants. This evidence supports hydrogen abstraction as a controlling step of antioxidant action. In fact, careful examination of Figure 1¹⁰ in the article by Boozer, Hammond, et al., which plots ml. of oxygen absorbed versus time in minutes for a normal and deuterated amine, shows tendencies toward an isotope effect. The induction period with the deuterated amine is longer than with the normal amine, and the initial rate of oxidation inhibited by deuterated amine is slightly greater than that observed with the normal amine.

The demonstration of a kinetic isotope effect in the present study does not rule out the formation of a π -complex or electron abstraction as possible reactions in the inhibition mechanism. With certain types of compounds, such as tertiary amines, where hydrogen abstraction cannot occur, these or other alternatives as the important step in antioxidant action seem highly probable. However, with typical rubber antioxidants of the secondary aryl amine and hindered phenol types where a labile hydrogen is present, the evidence indicates that hydrogen abstraction is the usual rate-controlling reaction in the mechanism of antioxidant action.

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Synopsis

The importance of hydrogen abstraction by peroxy radicals as a mechanism of anti-oxidant action in rubber has been studied by investigation of a deuterium isotope effect with amine and phenolic inhibitors in the oxidation of butadiene-styrene rubber. Deuterium was substituted for the active hydrogen of *N*-phenyl-2-naphthylamine and 2,6-di-*tert*-butyl-4-methylphenol by reacting the antioxidants with methylmagnesium iodide and then with deuterium oxide. The oxidation rates of butadiene-styrene polymer inhibited with 3 parts per hundred of these compounds were measured and compared with the oxidation rates using normal antioxidants. A kinetic isotope effect in the rate of oxidation was observed with both the phenolic inhibitor ($k_D/k_H = 1.3$ with not less than 77% substitution) and the amine inhibitor ($k_D/k_H = 1.8$ with not less than 60% substitution). The existence of an isotope effect leads to the conclusion that hydrogen donation to a peroxy radical is a controlling step in the mechanism by which these antioxidants function to retard the oxidation of rubber.

Résumé

L'importance de l'arrachement d'hydrogène au moyen de radicaux peroxydés, comme mécanisme de l'action anti-oxydante au sein du caoutchouc, a été étudiée au moyen de l'effet isotopique du deuterium avec des inhibiteurs aminés et phénoliques dans l'oxydation du caoutchouc de butadiène-styrène. Le deuterium était substitué à l'hydrogène actif de la *N*-phényl-2-naphthylamine et du 2,6-di-*tert*-butyl-4-méthylphénol en faisant réagir les antioxydants avec l'iodure de méthylmagnésium et ultérieurement avec l'oxyde de deuterium. Les vitesses d'oxydation du polymère butadiène-styrène, inhibée par 3% de ces composés, ont été mesurées et comparées aux vitesses d'oxydation en présence d'antioxydants habituels. On a observé un effet isotopique cinétique sur la vitesse d'oxydation aussi bien pour l'inhibiteur phénolique ($k_D/k_H = 1.3$ avec au moins 77% de substitution) que pour l'inhibiteur aminé ($k_D/k_H = 1.8$ avec au moins 60% de substitution). L'existence de cet effet isotopique amène à la conclusion que la cession d'un hydrogène à un radical peroxydé est déterminant de vitesse pour le mécanisme par lequel ces antioxydants agissent pour retarder l'oxydation du caoutchouc.

Zusammenfassung

Die Bedeutung des Wasserstoff-Abzuges durch Peroxyradikale als eine Mechanismus des Antioxydationsvorgangs in Kautschuk wurde durch Untersuchung einer Deuterium-Isotopreaktion mit Amin- und Phenol-Inhibitoren in der Oxydation von Butadien-Styrol-Kautschuk untersucht. Deuterium wurde für den aktiven Wasserstoff von *N*-Phenyl-2-naphthylamin und 2,6-di-*tert*-Butyl-4-methylphenol durch Reaktion der Antioxydationsmittel mit Methylmagnesiumjodid und daraufhin mit Deuteriumoxyd substituiert. Die Oxydationsgeschwindigkeiten von Butadien-Styrol-Polymer, welches imt drei Teilen pro Hundert dieser Verbindungen inhibiert war, wurden gemessen und mit den Oxydationsgeschwindigkeiten unter Benutzung normaler Antioxydationsmittel verglichen. Eine kinetische Isotropwirkung auf die Oxydationsgeschwindigkeit wurde mit dem Phenolinhibitor ($k_D/k_H = 1,3$ mit nicht weniger als 77% Substitution) und dem

Amininhibitor ($k_D/k_H = 1,8$ mit nicht weniger als 60% Substitution) beobachtet. Das Bestehen einer Isotopwirkung führt zu dem Schluss, dass Wasserstoffabgabe an ein Peroxyradikal eine kontrollierende Stufe in dem Vorgang ist, durch den diese Antioxydationsmittel wirken, um die Oxydation von Kautschuk zu verspäten.

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