

Inhibition of Organic Decompositions

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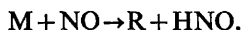
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Inhibitors such as nitric oxide and propylene act not by suppressing all chain processes, but by establishing other chain mechanisms in which the inhibitor is involved in both initiation and termination. Such inhibition is a special case of a general type of mechanism; sometimes an added substance increases the overall rate, sometimes it decreases it, and sometimes it leaves it unchanged. Initiation processes appear to involve atom abstraction (for example by the nitric oxide molecule, or by the allyl radical with propylene). Chain termination may involve interaction between a radical and a species involving the inhibitor. For nitric oxide it is proposed that species such as HNO and CH₃NO are involved in reactions with radicals. A number of cases are considered and applied to the available experimental evidence. Surface effects are considered, with special reference to the pyrolyses of organic halides.

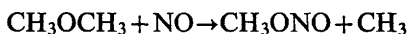
Recent work, some of which has been considered in previous publications,¹⁻³ has indicated that inhibited reactions are not molecular mechanisms but involve free-radical processes. The authors have previously suggested inhibition mechanisms in which the inhibitor is involved in both initiation and termination.¹⁻³ Mechanisms of this kind have been shown to be consistent with the experimental results in the inhibition of ethane^{2,3} propane,⁴ butane⁵ and dimethyl ether.⁶ Mechanisms for other reactions are being worked out in detail in this laboratory, and a number of different types of reaction mechanisms are involved. The object of the present paper is to consider under what circumstances these inhibition mechanisms apply.

INHIBITION BY NITRIC OXIDE

The initiating reaction that has been previously put forward^{1,3} in nitric oxide inhibition is of the type

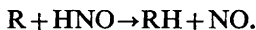


It is also possible that in some cases displacement reactions such as

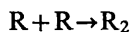


are involved. It is difficult to distinguish between these two possible initiating reactions, since they lead to the same kinetic behaviour; for simplicity it will be assumed that the first reaction is responsible for initiation.

If the decomposition is of such a nature that hydrogen atoms are involved in chain-propagating steps the concentration of HNO will be large since the bond strength $D(H-NO)$ is about 48 kcal.^{3,7} Under these circumstances the main chain-terminating step will involve the most plentiful radical R and the species HNO,

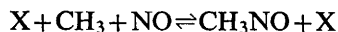


This reaction will predominate over



at sufficiently high concentrations of nitric oxide.

In systems in which hydrogen atoms are not chain carriers the concentration of H atoms and therefore of HNO will be very small. If R is a radical involved in chain-propagating steps, large concentrations of RNO may be present. If, for example, the methyl radical is a chain carrier, the equilibrium



will be established. The species CH_3NO , produced largely in vibrationally excited states, will readily undergo reaction of the type, $\text{R} + \text{CH}_3\text{NO} \rightarrow \text{RCH}_3 + \text{NO}$. It is to be noted that in this reaction the nitric oxide is essentially acting as a "chaperon" for the radical recombination, in the manner recently discussed by Porter.⁸

On the basis of the above considerations a typical inhibited decomposition mechanism may be written as follows:



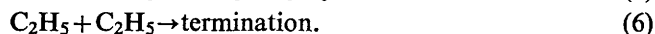
This is the scheme that has been proposed^{1,3} for the inhibited decomposition of ethane, and which with some modification applies to other paraffin hydrocarbons.^{4,5} The order of the overall reaction depends on whether the terminating reaction involves a μ radical,* as above, in which case the order is unity, or a β radical, in which case the order is 3/2. In order to establish whether the reaction in the presence of nitric oxide will be faster or slower than the uninhibited reaction one must write down the overall rate expressions for the inhibited and uninhibited cases. For ethane the rates are

$$v_{\text{inh.}} = (k_2 k_3 K)^{1/2} [\text{C}_2\text{H}_6] \quad (1)$$

and

$$v_{\text{uninh.}} = k_2 (2k_1/k_6)^{1/2} [\text{C}_2\text{H}_6], \quad (2)$$

where reactions (1) and (6) are



The constant K is the equilibrium constant for the reaction $\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}$. By substituting values for the rate constants it can be shown³ that the uninhibited rate is greater than the rate in the presence of nitric oxide.

This is not, however, a necessary result in mechanisms of this type. If ethane were to decompose by the mechanism.



the uninhibited rate would be

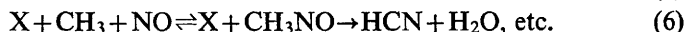
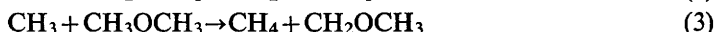
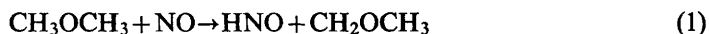
$$v_{\text{uninh.}} = (k_6 k_7 k_8 / k_9)^{1/2} [\text{C}_2\text{H}_6]. \quad (3)$$

The ratio $v_{\text{uninh.}}/v_{\text{inh.}}$ is readily shown to be equal to unity. This result shows that lack of inhibition by nitric oxide or any other substance must not be accepted as compelling evidence that a reaction proceeds by a molecular mechanism.

* A μ radical is one that is involved in first-order propagation reactions, a β radical one involved in second-order reactions.

This point is particularly worth emphasizing for the decomposition of alkyl halides. A mechanism involving $RX \rightarrow R + X$ as the initiation reaction and $R + X \rightarrow RX$ as the termination reaction gives rise to the same rate as one involving the corresponding processes $RX + NO \rightarrow R + XNO$ and $R + XNO \rightarrow RX + NO$.

An example of a mechanism in which there is termination by CH_3NO is the following ⁶:



In this particular case, termination involves the β radical CH_3 reacting with the species CH_3NO , which is of the general type βNO . The resulting rate expression is

$$v = k_3(k_1k_{-6}/k_6k_7)^{1/2}[CH_3OCH_3]^{3/2} + 2k_1[CH_3OCH_3][NO]. \quad (4)$$

This mechanism predicts an increase in rate at high nitric oxide concentrations, in agreement with experiment.

In table 1 the various possible chain-ending steps are considered, and the corresponding rate equation is given. The rate equations given in table 1 do not apply at lower nitric oxide concentrations than those giving rise to maximal inhibition. When nitric oxide is added to a system the net rate of initiation is increased, since the "uninhibited" initiation process is still taking place; moreover, at nitric oxide concentrations sufficient to give maximal inhibition the rate of the uninhibited initiation

TABLE 1.—SUMMARY OF RATE LAWS FOR REACTIONS INHIBITED BY NITRIC OXIDE

Initiation: $M + NO \rightarrow R + HNO$		
termination	rate equation at and after maximum inhibition	hydrogen atoms as chain carriers
$\beta + HNO$	$* v = k[M]^{3/2}$	yes
$\mu + HNO$	$v = k[M]$	yes
$\beta + \beta NO$	$v = k[M]^{3/2} + k'[M][NO]$	no
$\mu + \beta NO$	$v = k[M]$	no
$\beta + \mu NO$	$v = k[M]$	no
$\mu + \mu NO$	$v = k[M]^{1/2}$	no
$\beta + NO$	$v = k[M]^2 + k'[M][NO]$	no
$\mu + NO$	$v = k[M] + k'[M][NO]$	no

k' is generally twice the rate constant for the initiation reaction $M + NO \rightarrow HNO + R$.

* All the rate expressions have a $k'[M][NO]$ term; here only the terms which appear at low concentrations of inhibitor are included.

is smaller than the rate of initiation induced by nitric oxide. When the steady state is established the rate of termination must be equal to the rate of initiation. The concentration of HNO (or RNO) in the proposed mechanisms is large so that the concentration of the other radical R involved in termination (e.g., C_2H_5 in the ethane decomposition) must be correspondingly depressed in order for the rate of termination to be equal to the rate of initiation. Since R is a chain-carrying radical the rate is less than in the absence of nitric oxide. For a quantitative treatment of the reaction in the region of low nitric oxide concentrations, it is necessary to consider both modes

of initiation and both modes of termination; the resulting steady-state equations are then complicated (involving the solution of a cubic for ethane), but lead in the limiting cases to the equations for the uninhibited and maximally inhibited reactions.

It is seen from table 1 that some of the mechanisms lead directly to acceleration at high nitric-oxide concentrations. In all other cases there will also be acceleration at sufficiently high nitric-oxide concentrations, for the following reason. With ethane, for example, the concentration of HNO increases with the NO concentration, whereas that of C₂H₅ does not; the termination step HNO + HNO will therefore ultimately predominate. The rate expression then takes the form

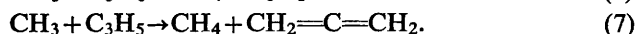
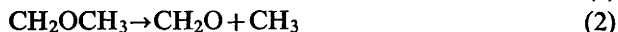
$$v = k_1[M][NO] + k[M]^2 + k'[M]^{3/2}/[NO]^{1/2}. \quad (5)$$

The rate is thus equal to $k_1[M][NO]$ at high nitric-oxide concentrations, in agreement with the results reported by Blackmore and Hinshelwood⁹ for a number of hydrocarbons.

INHIBITION BY OTHER SUBSTANCES

In some instances, propylene and other inhibitors give the same limiting rate as does nitric oxide. This result is readily explained on the basis of eqn. (1). Since this equation involves only quantities that do not depend upon the nature of the inhibitor it follows that the same rate will be obtained with any inhibitor that can become involved in the same type of mechanism. Specifically it is proposed^{1,2} that the allyl radical C₃H₅ plays the role of NO, and that C₃H₆ is involved in the chain-terminating step by reacting with radicals.

With mechanisms such as that proposed above for the dimethyl ether decomposition the situation is different. Addition of nitric oxide leads to inhibition followed by acceleration at higher inhibitor concentrations.⁶ The minimum rates for nitric oxide and for propylene inhibition are now significantly different, and in both cases the reactions are of three-halves order at the minima. Eqn. (4) shows that the mechanism is consistent with the facts for the nitric oxide inhibition. For the propylene-inhibited reaction the facts are accommodated by the following mechanism, which closely parallels that given above for nitric oxide:



The corresponding rate equation is

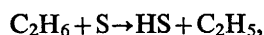
$$v = k_3 \left(\frac{k_4 k_1}{k_6 k_7} \right)^{\frac{1}{2}} [\text{CH}_3\text{OCH}_3]^{\frac{3}{2}} + \left(\frac{k_4 k_1 k_6}{k_7} \right)^{\frac{1}{2}} [\text{CH}_3\text{OCH}_3]^{\frac{1}{2}} [\text{C}_3\text{H}_6], \quad (6)$$

which is consistent, both qualitatively and quantitatively, with the experimental results.⁶ As with nitric oxide a number of chain-ending steps are possible for propylene-inhibited reactions.

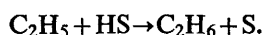
In some instances an added substance which gives rise to the same types of initiation and termination steps as indicated above may lead to a rate that is greater than for the uninhibited reaction. That H₂S acts in this way has been recently demonstrated.¹⁰

INFLUENCE OF SURFACE

The conclusion that added gases may become involved in reactions of the type discussed above calls for a reconsideration of the role of the surface in organic pyrolyses and other reactions. A surface site S may act like an NO molecule and abstract a hydrogen atom from a substrate molecule; the resultant species SH may bring about termination by reacting with radicals. A simple case to consider is that of the decomposition of ethane, in which initiation may occur in part as



and termination as

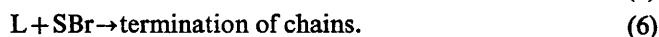


The role of S is thus exactly the same as that of NO, and inhibition by surface is to be expected; it is actually found.¹¹ In agreement with this point of view it is observed³ that the reaction inhibited by nitric oxide is less affected by surface than is the uninhibited reaction.

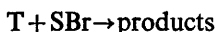
It was noted above that for certain reactions, including the decompositions of some alkyl halides, it is possible to formulate mechanisms in which nitric oxide is involved in initiation and termination but for which the rates are the same or similar as for the reaction in the absence of nitric oxide. In the same way (replacing NO by S and HNO by HS) one can arrive at a mechanism in which the surface is involved in both initiation and termination but which predicts no effect of surface on the over-all kinetics. It clearly cannot be concluded that a reaction is homogeneous from the fact that changing the surface:volume ratio, or changing the nature of the surface, has no effect on the rate.

These possibilities raise the important question of the significance of the "seasoning" of reaction vessels, a practice that has been carried out in particular in the study of the pyrolyses of organic halides. Such pyrolyses are particularly sensitive to the surface:volume ratio and to the state of the surface; as a result it is often difficult to obtain reproducible results. After a number of runs have been carried out in a given vessel, however, a carbonaceous film is deposited on the surface, and the rates—lower than initially—are then more reproducible. It has usually been assumed that seasoned vessels contain fewer active surface sites, and that heterogeneous processes are less important. An alternative—and in our opinion more likely—possibility is that carbonaceous films contain *more* active surface sites than clean glass surfaces. Reactions in seasoned vessels may therefore occur by mechanisms in which initiation and termination occur to a significant extent at the surface; they are therefore partially inhibited reactions, and are only slightly inhibited by nitric oxide.

In support of this point of view may be mentioned the fact that it is possible to predict the orders of reaction for bromide decompositions, all of them being regarded as taking place by free-radical mechanisms. As an example may be considered the decomposition of the various butyl bromides, for which the following mechanism is proposed:



In this scheme L is a radical having the free electron so placed that elimination of a bromine atom cannot occur (e.g., $\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HBr}$) and T is a radical that can eliminate a bromine atom (e.g., $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_2\text{Br}$). Application of the steady-state treatment to this mechanism leads to 3/2-order kinetics. If, on the other hand, the termination step is



the order is unity.

It is reasonable to postulate that the free radical that will be involved in termination (L or T) will be that in which the odd electron is on the terminal carbon atom. The situation for the four butyl bromides is shown in table 2, and it is predicted that the order will be $\frac{3}{2}$ with the normal and iso bromides, and unity with the secondary and tertiary compounds. The predictions are in agreement with experiment in all four cases. This interpretation is offered as an alternative to the assumption that the secondary and tertiary compounds decompose by molecular mechanisms.

TABLE 2.—DECOMPOSITION OF BUTYL BROMIDES

species	n-butyl	isobutyl	sec-butyl	tert-butyl
M	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	$(\text{CH}_2)_2\text{CHCH}_2\text{Br}$	$\text{CH}_3\text{CH}_2\text{CHBrCH}_3$	$(\text{CH}_3)_3\text{CBr}$
L	$\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HBr}$	$(\text{CH}_3)_2\text{CH}\dot{\text{C}}\text{HBr}$	$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{BrCH}_3$	—
T	$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_2\text{Br}$	$(\text{CH}_3)_2\dot{\text{C}}\text{CH}_2\text{Br}$	$\text{CH}_3\text{CH}_2\text{CHBr}\dot{\text{C}}\text{H}_2$	$(\text{CH}_3)_2(\dot{\text{C}}\text{H}_2)\text{CBr}$
termination step	$\text{L} + \text{SBr}$	$\text{L} + \text{SBr}$	$\text{T} + \text{SBr}$	$\text{T} + \text{SBr}$
over-all order	3/2	3/2	1	1

The authors are indebted to Dr. A. Maccoll and Mr. R. A. Ross for a valuable discussion of halide decompositions.

¹ Wojciechowski and Laidler, *Can. J. Chem.*, 1960, **38**, 1027.

² Laidler and Wojciechowski, *Proc. Roy. Soc. A*, 1960, **259**, 257.

³ Laidler and Wojciechowski, *Proc. Roy. Soc. A*, 1961, **260**, 103.

⁴ Laidler, Sagert and Wojciechowski, *Proc. Roy. Soc. A*, 1962, **270**, 242, 254.

⁵ Sagert and Laidler, *Can. J. Chem.*, in press.

⁶ Laidler, McKenney and Wojciechowski, *Can. J. Chem.*, in press.

⁷ Clement and Ramsay, *Can. J. Physics*, 1961, **39**, 205.

⁸ Porter, *Disc. Faraday Soc.*, 1962, **32**.

⁹ Blackmore and Hinshelwood, *Proc. Roy. Soc. A*, 1962, **268**, 21.

¹⁰ McKenney and Laidler, to be published; cf. Imai and Toyama, *Bull. Chem. Soc., Japan*, 1961, **34**, 328.

¹¹ Laidler and Wojciechowski, *Proc. Roy. Soc. A*, 1961, **260**, 91.