A Mechanism for the Decomposition of Ethylene Oxide

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## A Mechanism for the Decomposition of Ethylene Oxide

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The thermal decomposition of ethylene oxide exhibits an induction period, and is inhibited by the addition of inert gases. The assumptions that ethylene oxide mainly isomerizes to acetaldehyde, but at the same time produces free radicals which induce a chain decomposition of the acetaldehyde, and that the recombination of methyl radicals requires a third body lead to expressions for the length of the induction period and the pressure change during a run in qualitative agreement with experiments by Heckert and Mack.

THE thermal decomposition of ethylene oxide, studied by Heckert and Mack,[1] has a number of unusual features. The decomposition is homogeneous in Pyrex, and follows the equation

$$(CH_2)_2O = CH_4 + CO.$$
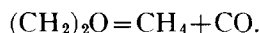
There is a pronounced "induction period," lasting about thirty minutes at 380°C, which decreases as the temperature is increased; the pressure-time curve is therefore S shaped. After the induction period is over the reaction is approximately first order. The addition of inert gases increases the induction period considerably, and decreases the rate of the reaction as a whole. The mechanism proposed by Heckert and Mack, the production of an excited acetaldehyde molecule, which then decomposes to $CH_4 + CO$ or is deactivated by collision, has been shown to be improbable by Kassel.[2]

Consideration of the structure of ethylene oxide indicates that the initial step of Heckert and Mack's mechanism, the conversion of ethylene oxide to acetaldehyde, is quite plausible, especially since an analogous reaction, the conversion of cyclopropane to propene, is known.[3] It is also known that if free radicals are introduced into acetaldehyde a chain decomposition of the acetaldehyde is set up,[4] which proceeds rapidly at a temperature considerably lower than that at which acetaldehyde will react alone. The isomerization of ethylene oxide to acetaldehyde accompanied by the production of a few free radicals would, therefore, lead to the observed reaction. It is the purpose of this paper to show that a mechanism of this sort will account for many of the features of the decomposition of ethylene oxide.

If we suppose, then, that ethylene oxide usually reacts by forming acetaldehyde, but that occasionally a free radical is formed which reacts with acetaldehyde just as methyls do, we can set up the following sequence of reactions:[5]
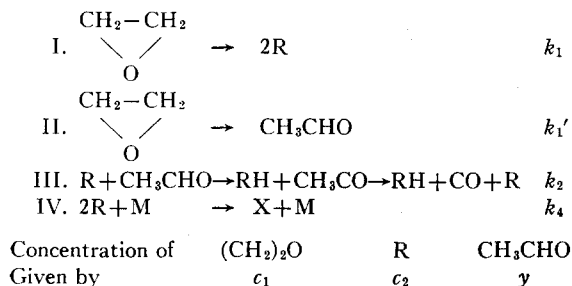
[1] Heckert and Mack, J. Am. Chem. Soc. **51**, 2706 (1929).
[2] Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalog Co., 1932), p. 284.
[3] Chambers and Kistiakowsky, J. Am. Chem. Soc. **56**, 399 (1934).
[4] Allen and Sickman, J. Am. Chem. Soc. **56**, 2031 (1934).
[5] All free radicals are denoted by R, and are assumed to react in the same way; the main chain carrier presumably is, however, the methyl radical produced by II. The chain breaking step IV is assumed to require a third body M, whose effect is absorbed in the rate constant k_4.

I.
$$
\begin{array}{c}
CH_2\!-\!CH_2 \\
\diagdown\;\diagup \\
O
\end{array}
\quad \rightarrow \quad 2R \qquad\qquad k_1
$$

II.
$$
\begin{array}{c}
CH_2\!-\!CH_2 \\
\diagdown\;\diagup \\
O
\end{array}
\quad \rightarrow \quad CH_3CHO \qquad k_1'
$$

III. $R + CH_3CHO \rightarrow RH + CH_3CO \rightarrow RH + CO + R$ $\quad k_2$
IV. $2R + M \quad\rightarrow\quad X + M$ $\qquad\qquad k_4$

Concentration of	$(CH_2)_2O$	R	CH_3CHO
Given by	c_1	c_2	y

Following Rice and Herzfeld,[6] a steady state equation for the concentration of free radicals may be set up,

$$
dc_2/dt = 2k_1c_1 - 2k_4c_2{}^2 = 0, \qquad (1)
$$

or

$$
c_2 = (k_1c_1/k_4)^{\frac{1}{2}}. \qquad (2)
$$

The rate at which ethylene oxide disappears is given by

$$
-dc_1/dt = k_1c_1 + k_1'c_1 = \kappa c_1, \qquad (3)
$$

where

$$
\kappa = k_1 + k_1' \cong k_1' \quad \text{if} \quad k_1 \ll k_1'. \qquad (4)
$$

The concentration of ethylene oxide at any time t is given by integrating (3), which gives, if A is the initial concentration of ethylene oxide,

$$
c_1 = A \exp(-\kappa t). \qquad (5)
$$

Now acetaldehyde is being formed and decomposed at the same time by reactions II and III; its net rate of formation is given by

$$
\begin{aligned}
dy/dt &= k_1'c_1 - k_2c_2y = k_1'c_1 - k_2(k_1c_1/k_4)^{\frac{1}{2}}y \\
&= k_1'A \exp(-\kappa t) - k_2(k_1A/k_4)^{\frac{1}{2}} \\
&\qquad\qquad \times \exp(-\kappa t/2)y, \quad (6)
\end{aligned}
$$

by substituting for c_1 from (5).

It is now convenient to set $\exp(-\kappa t/2) = x$, which maps the t axis from zero to infinity on the x axis from one to zero. Eq. (6) becomes

$$
\begin{aligned}
dy/dx &= -2k_1'Ax/\kappa + 2k_2y(k_1A/k_4)^{\frac{1}{2}}/\kappa \\
&= -Qx + Py, \qquad\qquad\qquad\qquad (7)
\end{aligned}
$$

where

$$
P = 2k_2(k_1A/k_4)^{\frac{1}{2}}/\kappa \quad \text{and} \quad Q = 2k_1'A/\kappa \cong 2A. \qquad (8)
$$

The integral of this equation, giving the concentration of aldehyde at any time, or rather x value, during a run, remembering that at $t = 0$,

---

$x = 1$ and $y = 0$, is

$$
y = Q/P^2\{1 + Px - (1+P)\exp[-P(1-x)]\}. \qquad (9)
$$

The concentration of aldehyde given by this equation has a maximum during a run given by setting $dy/dx = 0$. The x value at which y reaches this maximum is

$$
x^* = 1 - (1/P)\log(1+P). \qquad (10)
$$

Finally, the total pressure p during the run is given by

$$
\begin{aligned}
p &= c_1 + y + 2(A - c_1 - y) = 2A - c_1 - y \\
&= 2A - Ax^2 - 2A/P^2\{1 + Px \\
&\qquad\qquad - (1+P)\exp[-P(1-x)]\}. \quad (11)
\end{aligned}
$$

This expression is easily seen to have the form given by the experimental data, and the latter may be used to get an idea of the magnitude of the constant P.

The value of x^* is that given by the inflection point in the pressure-time curve for the reaction.[7] For Heckert and Mack's[1] run 168m ($A = 107.42$ cm) this is about 30 minutes, and with their k_1 as κ, $P \cong 190$.

Furthermore, P should have a positive temperature coefficient, so that raising the temperature will increase P. From (10) we see that increasing P increases x^*, and thus shortens the induction period, as is found experimentally.

INERT CASES

So far we have neglected the assumption that reaction IV requires a third body and that k_4 depends on the concentration of everything present in the reaction vessel, which precludes the possibility that (11) will hold exactly. According to the scheme presented,[8] the only effect of

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[7] This is not exactly true, as x^* as defined here is the inflection point of the p, x curve, which is not identical with that of the p, t curve. Strictly, P should be calculated from the equation $1 - x' = (1/P)\log(1 + P + Px' + P^2x')/(2Px' + 1)$ obtained by setting $d^2p/dt^2 = 0$, where x' is the x value of the inflection point on the p, t curve. Since $P \gg 1$,

$$
x' \cong 1 - (1/P)\log(P/2) \cong x^* + (1/P)\log 2,
$$

and P becomes 160 instead of 190 as above.

[8] I and II are assumed unimolecular and first order. If they have "fallen off" to any considerable extent the effect of adding inert gases will be decreased, as I and II will then be increased simultaneously with IV. The further modifications necessary in this case are easily made. Experimentally, P decreases with increasing A but κ remains almost constant, so that apparently k_1 has fallen off considerably.

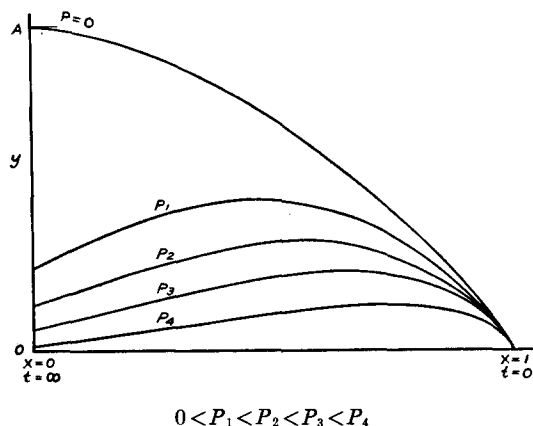[6] F. O. Rice and Herzfeld, J. Am. Chem. Soc. 56, 284 (1934).

$$0 < P_1 < P_2 < P_3 < P_4$$

FIG. 1. Schematic diagram of the concentration of aldehyde y as a function of the "time function" $x = \exp(-\kappa t/2)$.

adding inert gas will be to increase k_4, and therefore to decrease P. That decreasing P increases the induction period has already been pointed out; the general effect of changing P may be seen from the following.

Consider dy/dx for two values of P, P_1 and P_2, where $P_1 > P_2$, all other quantities being the same, and let the corresponding values of y be y_1 and y_2. Then

$$dy_1/dx - P_1 y_1 = -Qx, \qquad \text{(a)}$$

$$dy_2/dx - P_2 y_2 = -Qx. \qquad \text{(b)}$$

Subtracting (b) from (a) and adding $P_1 y_2$ to each side we get

$$d(y_1 - y_2)/dx - P_1(y_1 - y_2) = (P_1 - P_2)y_2.$$

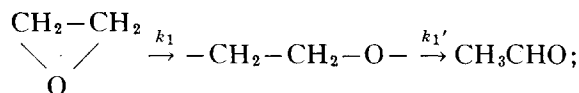Now set $z = y_1 - y_2$, and multiply each side by $\exp(-P_1 x)$. Then

$$(dz/dx - P_1 z)\exp(-P_1 x)$$
$$= (P_1 - P_2)y_2 \exp(-P_1 x). \quad \text{(c)}$$

The left-hand side of (c) is equal to $d[z \exp(-P_1 x)]/dx$ and the right-hand side is positive for $0 < x < 1$. The function $z \exp(-P_1 x)$ is therefore a monatonic increasing function of x. Now when $x = 1$, $y_1 = y_2 = 0$, and therefore $z = z \exp(-P_1 x) = 0$, so that for all $x < 1$, $z \exp(-P_1 x)$ is negative, and since $\exp(-P_1 x)$ is always positive, $z = y_1 - y_2 < 0$, or $y_2 > y_1$. Thus

if P is decreased y is increased at all times during the run. Fig. 1 is a schematic diagram of y as a function of x for different values of P. An increase of y means a corresponding decrease in the observed pressure, and adding inert gas should therefore decrease the rate of the reaction, again in agreement with experiment.

THE INITIAL REACTION

If, as seems reasonable, we can identity κ with k_1', we can draw some conclusions as to the mechanism of reactions I and II. Heckert and Mack[2] find $k_1' = 10^{13} \exp(-5200/RT)$ sec.$^{-1}$. This is definitely in favor of a bond breaking mechanism[9] such as

$$\begin{array}{c} CH_2 - CH_2 \\ \diagdown \quad \diagup \quad \xrightarrow{k_1} -CH_2 - CH_2 - O - \xrightarrow{k_1'} CH_3CHO; \\ O \end{array}$$

the "2R" of I would then be $-CH_2-CH_2-O-$. This mechanism assumes that the ring opens only at the $C-O$ bond. An equally plausible mechanism would be to assume that the $-CH_2-CH_2-O-$ radical rearranges at once to acetaldehyde, but that occasionally the ring opens at the $C-C$ bond, giving $-CH_2-O-CH_2-$. This radical might then react as the "2R" of I, or it might split off CH_2O, forming a CH_2. In any case the mathematical equations would be unchanged.

THE RECOMBINATION OF METHYL RADICALS

F. O. Rice and Herzfeld[6] assume that methyls recombine by a bimolecular association, while the mechanism assumed here requires a three-body reaction, which also seems preferable theoretically. It should be pointed out, however, that the chain decomposition of acetaldehyde induced by azomethane[4] seems to be consistent with a bimolecular association. The implications of IV requiring a third body in other reactions will be discussed elsewhere.

[9] O. K. Rice and Gershinowitz, J. Chem. Phys. 3, 485 (1935).