Modeling for Vapor-Phase Nitration of Ethane and Propane with Nitrogen Dioxide at Lower Temperatures

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Modeling for the vapor-phase nitrations of C_2H_6 and C_3H_8 with NO_2 at 140-220℃ has been studied. Two reaction models which might describe our previous experimental results have been presented and then their validity has been estimated by comparing the concentration behavior of the significant compounds calculated from these models with that obtained experimentally. The results showed that these two models could elucidate the behavior of the main compounds almost quantitatively in spite of the fact that the nitrations should be very complicated systems containing a great many elementary reactions.

Some trials for quantitative interpretation on the nitration mechanism by using these models suggested that NO_2 radical should be the most important species for hydrogen abstraction from the paraffins and that in the nitration of C_2H_6, CH_3 radical should be mainly produced from C_2H_5O radical through CH_3CHO, CH_3COONO and CH_3COO radical.

1. Introduction

The vapor-phase nitration of paraffins is a most interesting one from both a theoretical and an engineering standpoint, and hence a number of investigations have been carried out since about 1930[1]. We also presented previously some papers on it[2)~6)]. Although the mechanistic aspects of the vapor-phase nitration seem to be well understood qualitatively, there are many important details that still need to be investigated before a complete quantitative understanding of the nitration is possible. Some important mechanistic problems such as radicals involving hydrogen abstraction from paraffins, one of the most significant reactions, main reaction paths to give nitroparaffins and other products, and a possibility of producing nitroparaffins due to chain reactions have been suggested and discussed by many investigators[1)3)4)7)~14)]. However, it is very difficult to explain such problems quantitatively because the nitration in a very complicated system containing a great many elementary reactions, and therefore any available procedures for analyzing such a complicated system and reliable information on their rate parameters have not yet obtained.

Several numerical techniques used to integrate the system of differential equations have recently been found to be very useful for expressing the concentration behavior of all the species in such a complicated system as air pollution[15]. Many but not so sufficient rate constants of the elementary reactions involving the nitration have also been published[16]. We would therefore try to present reaction models which might be able to de-

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scribe the concentration behavior of the main compounds in the nitration, based on some reaction schemes previously suggested[1] and current rate constants[16]. In addition, we would try to explain some problems described above quantitatively by using these models.

In this work we restrict ourselves to modeling for the nitrations of C_2H_6 and C_3H_8 with NO_2 at lower temperatures such as 140—200℃. Although modeling for the nitrations of the paraffins with HNO_3 at higher temperatures such as about 400 ℃ is very interesting from both an industrial and a mechanistic standpoint, it might be difficult to estimate the validity of the models without having some stepwise investigations due to following reasons;

1. It might be difficult to obtain the concentration behavior of the main products experimentally because of very fast reactions.
2. The reaction system might become much more complicated.

On the other hand, it may be more easy to carry out the modeling for the nitration at lower temperatures because the models include much few reactions and because it will be possible to estimate their validity sufficiently by comparing the concentration behavior of the main products calculated from these models with that obtained experimentally[3].

2. Reaction Model

From our previous experiments on the vapor-phase nitrations of C_2H_6 and C_3H_8 with NO_2 at lower temperature[3], the concentration behavior of the significant intermediates and products in the systems has already been obtained. Thus we presented two reaction models which might elucidate our previous experimental results for the nitrations of C_2H_6 and C_3H_8[3], referring to some previous informations on the nitration mechanism[1], selecting the necessary reactions, and adopting their reliable rate parameters.

Table 1 and 2 show the reaction models for the nitrations of C_2H_6 and C_3H_8 with NO_2, respectively. The validity of these two models was estimated by comparing the time variations of the significant compounds calculated by the models with those obtained in our experiments. AKITAC SYSTEM[17], one of the methods of quasi-steady state approximations, was used for the calculations. All the calculations were performed on a HITAC 8800/8700 computer at the Computer Centre, the University of Tokyo.

3. Results and Discussion

3.1. Validity of Reaction Models

3.1.1. Nitration Model of C_2H_6

Fig. 1 shows the concentration behavior of the significant compounds calculated from the model in Table 1 and that observed experimentally in

Table 1 Reaction model for the nitration of C_2H_6 with NO_2 at lower temperature

	Reaction		Log A	E	Ref.
(E- 1)	$C_2H_6 + {}^{\bullet}NO_2$	$= C_2H_5{}^{\bullet} + HNO_2$	10.5	27.9	31
(E- 2)	$C_2H_6 + C_2H_5O^{\bullet}$	$= C_2H_5{}^{\bullet} + C_2H_5OH$	9.00	7.4	18)
(E- 3)	$C_2H_6 + CH_3O^{\bullet}$	$= C_2H_5{}^{\bullet} + CH_3OH$	8.48	7.1	19)
(E- 4)	$C_2H_5{}^{\bullet} + {}^{\bullet}NO_2$	$= C_2H_5NO_2$	9.30	0	20)
(E- 5)	$C_2H_5{}^{\bullet} + {}^{\bullet}NO_2$	$= C_2H_5O^{\bullet} + NO$	9.48	0	20)
(E- 6)	$C_2H_5{}^{\bullet} + {}^{\bullet}NO$	$= C_2H_5NO$	9.00	0	20)
(E- 7)	$C_2H_5O^{\bullet} + {}^{\bullet}NO_2$	$= C_2H_5ONO_2$	9.90	0	21)
(E- 8)	$C_2H_5O^{\bullet} + {}^{\bullet}NO_2$	$= CH_3CHO + HNO_2$	9.60	0	21)
(E- 9)	$C_2H_5O^{\bullet} + {}^{\bullet}NO$	$= C_2H_5ONO$	10.3	0	21)
(E-10)	$C_2H_5O^{\bullet} + {}^{\bullet}NO$	$= CH_3CHO + HNO$	10.4	0	21)
(E-11)	$C_2H_5O^{\bullet}$	$= CH_3{}^{\bullet} + HCHO$	15.0	21.6	22)
(E-12)	$C_2H_5CHO_2$	$= C_2H_5O^{\bullet} + {}^{\bullet}NO_2$	16.0	40.4	21)
(E-13)	C_2H_5ONO	$= C_2H_5O^{\bullet} + {}^{\bullet}NO$	16.0	42.2	21)
(E-14)	$C_2H_5OH + {}^{\bullet}NO_2$	$= CH_3C^{\bullet}HOH + HNO_2$	9.30	22.9	26)
(E-15)	$CH_3C^{\bullet}HOH + {}^{\bullet}NO_2$	$= CH_3CHO + HNO_2$	9.60	0	21)
(E-16)	$CH_3C^{\bullet}HOH + {}^{\bullet}NO$	$= CH_3CHO + HNO$	7.00	0	21)
(E-17)	$CH_3CHO + {}^{\bullet}NO_2$	$= CH_3C^{\bullet}O + HNO_2$	9.00	19.9	27)
(E-18)	$CH_3C^{\bullet}O$	$= CH_3{}^{\bullet} + CO$	10.3	15.2	28)
(E-19)	$CH_3C^{\bullet}O + {}^{\bullet}NO_2$	$= CH_3C(O)ONO$	8.30	0	29)
(E-20)	$CH_3C^{\bullet}O + {}^{\bullet}NO$	$= CH_3C(O)NO$	8.30	0	29)
(E-21)	$CH_3C(O)ONO$	$= CH_3C(O)O^{\bullet} + {}^{\bullet}NO$	16.7	42.2	21)
(E-22)	$CH_3C(O)NO$	$= CH_3C^{\bullet}O + {}^{\bullet}NO$	17.6	61.2	23)
(E-23)	$CH_3C(O)O^{\bullet}$	$= CH_3{}^{\bullet} + CO_2$	14.0	5.1	30)
(E-24)	$CH_3{}^{\bullet} + {}^{\bullet}NO_2$	$= CH_3NO_2$	9.30	0	20)
(E-25)	$CH_3{}^{\bullet} + {}^{\bullet}NO_2$	$= CH_3O^{\bullet} + NO$	9.48	0	20)
(E-26)	$CH_3{}^{\bullet} + {}^{\bullet}NO$	$= CH_3NO$	9.00	0	20)
(E-27)	$CH_3O^{\bullet} + {}^{\bullet}NO_2$	$= CH_3ONO_2$	9.70	0	24)
(E-28)	$CH_3O^{\bullet} + {}^{\bullet}NO_2$	$= HCHO + HNO_2$	8.70	0	24)
(E-29)	$CH_3O^{\bullet} + {}^{\bullet}NO$	$= CH_3ONO$	10.1	0	24)
(E-30)	$CH_3O^{\bullet} + {}^{\bullet}NO$	$= HCHO + HNO$	9.90	0	24)
(E-31)	CH_3ONO_2	$= CH_3O^{\bullet} + {}^{\bullet}NO_2$	15.7	40.9	24)
(E-32)	CH_3ONO	$= CH_3O^{\bullet} + {}^{\bullet}NO$	15.8	41.6	24)
(E-33)	$CH_3OH + {}^{\bullet}NO_2$	$= C^{\bullet}H_2OH + HNO_2$	9.49	28.2	26)
(E-34)	$C^{\bullet}H_2OH + {}^{\bullet}NO_2$	$= HCHO + HNO_2$	10.0	0	24)
(E-35)	$C^{\bullet}H_2OH + {}^{\bullet}NO$	$= HCHO + HNO$	10.0	0	24)
(E-36)	$HCHO + {}^{\bullet}NO_2$	$= HC^{\bullet}O + HNO_2$	9.00	19.0	27)
(E-37)	$HC^{\bullet}O + {}^{\bullet}NO_2$	$= CO + HNO_2$	9.00	0	31)
(E-38)	$HC^{\bullet}O + {}^{\bullet}NO$	$= CO + HNO$	10.6	0	32)
(E-39)	$C_2H_5NO + 2{}^{\bullet}NO$	$= C_2H_5{}^{\bullet} + N_2 + {}^{\bullet}NO_3$	0.28	-2.9	33)
(E-40)	$CH_3NO + 2{}^{\bullet}NO$	$= CH_3{}^{\bullet} + N_2 + {}^{\bullet}NO_3$	0.41	-1.0	33)
(E-41)	$2{}^{\bullet}NO + {}^{\bullet}NO_3$	$= 2{}^{\bullet}NO_2$	9.62	1.7	34)
(E-42)	$2HNO_2$	$= H_2O + {}^{\bullet}NO + {}^{\bullet}NO_2$	10.1	10.0	35)
(E-43)	$H_2O + {}^{\bullet}NO + {}^{\bullet}NO_2$	$= 2HNO_2$	4.33	0	35)

A: sec^{-1}(1st order), l/mol·sec(2nd order), l^2/mol^2·sec(3rd order)
E: kcal/mol

Table 2 Reaction model for the nitration of C_3H_8 with NO_2 at lower temperature

	Reaction		Log A	E	Ref.
(P- 1)	$C_3H_8 + {}^{\bullet}NO_2$	$= n\text{-}C_3H_7{}^{\bullet} + HNO_2$	10.6	27.9	3)
(P- 2)	$C_3H_8 + {}^{\bullet}NO_2$	$= i\text{-}C_3H_7{}^{\bullet} + HNO_2$	9.71	24.3	3)
(P- 3)	$C_3H_8 + n\text{-}C_3H_7O^{\bullet}$	$= n\text{-}C_3H_7{}^{\bullet} + n\text{-}C_3H_7OH$	9.78	7.1	18)
(P- 4)	$C_3H_8 + n\text{-}C_3H_7O^{\bullet}$	$= i\text{-}C_3H_7{}^{\bullet} + n\text{-}C_3H_7OH$	9.30	5.2	18)
(P- 5)	$C_3H_8 + i\text{-}C_3H_7O^{\bullet}$	$= n\text{-}C_3H_7{}^{\bullet} + i\text{-}C_3H_7OH$	9.78	7.1	18)
(P- 6)	$C_3H_8 + i\text{-}C_3H_7O^{\bullet}$	$= i\text{-}C_3H_7{}^{\bullet} + i\text{-}C_3H_7OH$	9.30	5.2	18)
(P- 7)	$n\text{-}C_3H_7{}^{\bullet} + {}^{\bullet}NO_2$	$= n\text{-}C_3H_7NO_2$	9.28	0	20)
(P- 8)	$n\text{-}C_3H_7{}^{\bullet} + {}^{\bullet}NO_2$	$= n\text{-}C_3H_7O^{\bullet} + NO$	9.46	0	20)
(P- 9)	$i\text{-}C_3H_7{}^{\bullet} + {}^{\bullet}NO_2$	$= i\text{-}C_3H_7NO_2$	9.28	0	20)
(P-10)	$i\text{-}C_3H_7{}^{\bullet} + {}^{\bullet}NO_2$	$= i\text{-}C_3H_7O^{\bullet} + NO$	9.46	0	20)
(P-11)	$n\text{-}C_3H_7{}^{\bullet} + {}^{\bullet}NO$	$= n\text{-}C_3H_7NO$	9.00	0	20)
(P-12)	$i\text{-}C_3H_7{}^{\bullet} + {}^{\bullet}NO$	$= i\text{-}C_3H_7NO$	9.00	0	20)
(P-13)	$n\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO_2$	$= n\text{-}C_3H_7ONO_2$	10.0	0	24)
(P-14)	$n\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO_2$	$= C_2H_5CHO + HNO_2$	9.18	0	24)
(P-15)	$i\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO_2$	$= i\text{-}C_3H_7ONO_2$	10.0	0	24)
(P-16)	$i\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO_2$	$= CH_3COCH_3 + HNO_2$	9.18	0	24)
(P-17)	$n\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO$	$= n\text{-}C_3H_7NO$	10.5	0	22)
(P-18)	$n\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO$	$= C_2H_5CHO + HNO$	10.4	0	22)
(P-19)	$i\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO$	$= i\text{-}C_3H_7NO$	10.5	0	25)
(P-20)	$i\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO$	$= CH_3COCH_3 + HNO$	10.4	0	25)
(P-21)	$n\text{-}C_3H_7ONO$	$= n\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO$	16.2	41.0	22)
(P-22)	$i\text{-}C_3H_7ONO$	$= i\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO$	16.2	41.0	25)
(P-23)	$n\text{-}C_3H_7ONO_2$	$= n\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO_2$	16.0	40.0	24)
(P-24)	$i\text{-}C_3H_7ONO_2$	$= i\text{-}C_3H_7O^{\bullet} + {}^{\bullet}NO_2$	16.0	40.0	24)
(P-25)	$n\text{-}C_3H_7OH + {}^{\bullet}NO_2$	$= C_2H_5C^{\bullet}HOH + HNO_2$	9.80	22.9	26)
(P-26)	$i\text{-}C_3H_7OH + {}^{\bullet}NO_2$	$= (CH_3)_2C^{\bullet}OH + HNO_2$	9.50	19.0	26)
(P-27)	$C_2H_5C^{\bullet}HOH + {}^{\bullet}NO_2$	$= C_2H_5CHO + HNO_2$	9.60	0	21)
(P-28)	$(CH_3)_2C^{\bullet}OH + {}^{\bullet}NO_2$	$= CH_3COCH_3 + HNO_2$	9.60	0	21)
(P-29)	$C_2H_5C^{\bullet}HOH + {}^{\bullet}NO$	$= C_2H_5CHO + HNO$	7.00	0	21)
(P-30)	$(CH_3)_2C^{\bullet}OH + {}^{\bullet}NO$	$= CH_3COCH_3 + HNO$	7.00	0	21)
(P-31)	$n\text{-}C_3H_7NO + 2{}^{\bullet}NO$	$= n\text{-}C_3H_7{}^{\bullet} + N_2 + {}^{\bullet}NO_2$	-2.30	-7.0	33)
(P-32)	$i\text{-}C_3H_7NO + 2{}^{\bullet}NO$	$= i\text{-}C_3H_7{}^{\bullet} + N_2 + {}^{\bullet}NO_2$	-0.70	-4.0	33)
(P-33)	${}^{\bullet}NO + {}^{\bullet}NO_2$	$= 2{}^{\bullet}NO_2$	9.62	1.7	34)
(P-34)	$2HNO_2$	$= H_2O + {}^{\bullet}NO + {}^{\bullet}NO_2$	10.4	10.0	35)
(P-35)	$H_2O + {}^{\bullet}NO + {}^{\bullet}NO_2$	$= 2HNO_2$	4.33	0	35)

A: sec^{-1}(1st order), $l/mol \cdot sec$(2nd order), $l^2/mol^2 \cdot sec$(3rd order)
E: kcal/mol

the nitration of C_2H_6 with NO_2 under typical conditions[3]. As can be seen from Fig. 1, the behavior of $C_2H_5NO_2$ and CH_3NO_2 as main final products and that of $C_2H_5ONO_2$ as a main intermediate obtained experimentally can be well explained by this model.

Fig. 2 shows variations of the concentration behavior of $C_2H_5NO_2$ with temperature under the same conditions as in Fig. 1 except for temperature. At 170—200℃ the behavior of $C_2H_5NO_2$ calculated can also explain experimental data well, while at 220℃ it can explain the data until the middle of the reaction period but it can not explain after that. These results suggest that at higher temperature some reactions which are not included in this model might be involved after the middle of the reaction period. However, on the whole this model might describe experimental

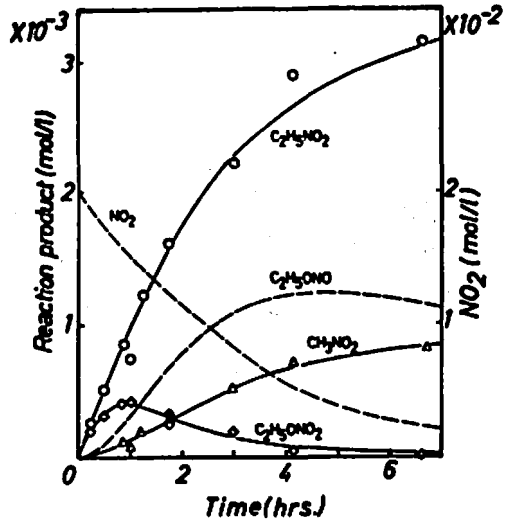


Fig. 1 Concentration behavior of significant compounds in the nitration of C_2H_6 with NO_2 at 185℃
$[C_2H_6]_0 : 5\times10^{-2}$mol/l
○△◇ : experimental, ---- : calculated

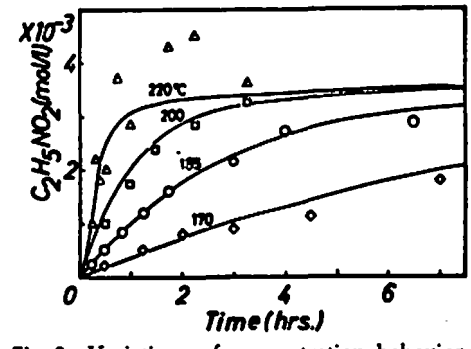


Fig. 2 Variations of concentration behavior of $C_2H_5NO_2$ with temperature in the nitration of C_2H_6 with NO_2
$[C_2H_6]_0 : 5\times10^{-2}$mol/l, $[NO_2]_0 : 2\times10^{-2}$mol/l
△□○◇ : experimental, —— : calculated

results well in spite of the complicated system containing a great many reactions.

3.1.2. Nitration Model of C_3H_8

Fig. 3 shows the concentration behavior of the significant compounds calculated from the model in Table 2 and that observed experimentally in the nitration of C_3H_8 with NO_2 under typical conditions[3]. The behavior of $i\text{-}C_3H_7NO_2$, $n\text{-}C_3H_7NO_2$ and CH_3COCH_3, the main products, observed experimentally in this system can be well explained by this model.

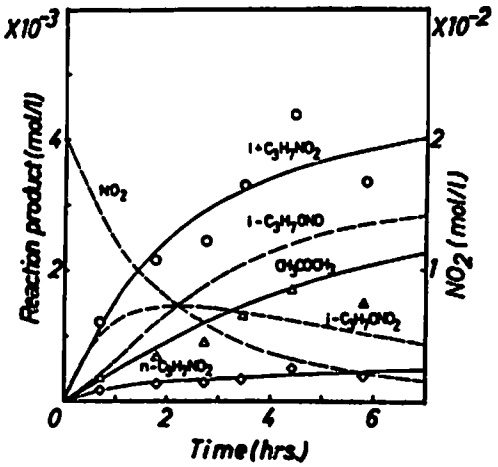


Fig. 3 Concentration behavior of significant compounds in the nitration of C_3H_8 with NO_2 at 159℃
$[C_3H_8]_0$: 5×10^{-2}mol/l
○△◇ : experimental, ---- : calculated

3.2 Relative Importance for Each Reaction Path

It has become clear that the behavior of the main products in the nitrations of C_2H_6 and C_3H_8 with NO_2 at lower temperatures could be well elucidated by these two models presented.

Therefore, the active species involving hydrogen abstraction from the paraffins and the main paths to give rise to the significant products have been discussed by comparing the rates of the competing reactions calculated from these models.

3.2.1 Active Species Involving Hydrogen Abstraction from Paraffins

NO_2 radical is well known to serve as a main species for hydrogen abstraction from paraffins in the nitrations of paraffins with NO_2[1]. There is a possibility that, in addition to this NO_2 radical, alkoxyl radicals produced in the reaction of alkyl radical with NO_2 radical might also take part in hydrogen abstraction as the nitration proceeds to some extent. Therefore, in order to clarify the relative contribution of these species to hydrogen abstraction, their rates have been calculated from these models.

Table 3 and 4 show variations of the concentrations of NO_2 and alkoxyl radicals and those of the abstraction rates by these radicals with time under typical nitration conditions of C_2H_6 and C_3H_8, respectively. As can be seen from Table 3 and 4, in the both nitrations the abstraction rates by NO_2 radical are much greater than those by alkoxyl radicals during all the course of reaction because of much lower concentrations of alkoxyl radicals in spite of their larger rate constants. These results suggest that NO_2 radical should be the most important species for hydrogen abstraction from the paraffins.

Then, the effects of the hydrogen abstraction rate from the paraffins by NO_2 radical on overall reactions have been examined. Fig. 4 shows variations of the concentration behavior of the main products with k_{E-1}, the rate constant of hydrogen abstraction from C_2H_6 by NO_2 radical, in the nitration of C_2H_6 with NO_2 under typical conditions. It can be seen that the hydrogen abstraction rate has a remarkable influence on the behavior of the main products, especially $C_2H_5NO_2$ and C_2H_5ONO. These facts suggest that hydrogen abstraction should be a most important step which influences

Table 3 Hydrogen abstraction rate from C_2H_6 by various radicals in the nitration of C_2H_6 with NO_2 at 185℃
$[C_2H_6]_0$: 5×10^{-2}mol/l, $[NO_2]_0$: 2×10^{-2}mol/l

Time (hrs.)		0	0.5	1.0	2.0	4.0	6.0	8.0
Concentration (mol/l)								
NO_2	(10^{-3})	20	17	16	13	5.7	2.9	1.6
$C_2H_5O^*$	(10^{-15})	—	2.4	2.0	1.5	1.3	1.3	1.2
CH_3O^*	(10^{-16})	—	5.5	7.2	8.6	12	14	15
C_2H_6	(10^{-2})	5.0	4.9	4.8	4.6	4.3	4.2	4.2
Reaction rate (mol/l·sec)								
$k_{E-1}[C_2H_6][NO_2]$	(10^{-8})	87	69	61	48	20	10	5.6
$k_{E-2}[C_2H_6][C_2H_5O^*]$	(10^{-11})	—	3.7	2.9	2.1	1.7	1.6	1.6
$k_{E-3}[C_2H_6][CH_3O^*]$	(10^{-12})	—	3.4	4.4	5.1	6.5	7.6	8.3

$k_{E-1}=8.2\times10^{-4}$, $k_{E-2}=3.1\times10^{5}$, $k_{E-3}=1.3\times10^{5}$ (l/mol·sec)

Table 4 Hydrogen abstraction rate from C_3H_8 by various radicals in the nitration of C_3H_8 with NO_2 at 159℃

$[C_3H_8]_0$:5×10^{-2}mol/l, $[NO_2]$: 2×10^{-2}mol/l

Time(hrs.)	0	0.5	1.0	2.0	4.0	6.0	8.0
Concentration(mol/l)							
$^{\bullet}NO_2$ (10^{-3})	20	17	16	13	5.7	2.9	1.6
$n\text{-}C_3H_7O^{\bullet}$ (10^{-16})	--	2.6	2.3	2.0	2.1	2.3	2.7
$i\text{-}C_3H_7O^{\bullet}$ (10^{-15})	—	2.2	1.9	1.7	1.7	2.0	2.3
C_3H_8 (10^{-2})	5.0	4.7	4.6	4.3	4.0	3.9	3.8
Reaction rate(mol/l·sec)							
formation of $n\text{-}C_3H_7{}^{\bullet}$:							
$k_{p-1}[C_3H_8][^{\bullet}NO_2]$ (10^{-8})	18	13	9.8	5.9	2.6	1.5	0.95
$k_{p-3}[C_3H_8][n\text{-}C_3H_7O^{\bullet}]$ (10^{-11})	--	2.0	1.7	1.4	1.3	1.5	1.7
$k_{p-5}[C_3H_8][i\text{-}C_3H_7O^{\bullet}]$ (10^{-10})	--	1.7	1.4	1.2	1.1	1.2	1.4
formation of $i\text{-}C_3H_7{}^{\bullet}$:							
$k_{p-2}[C_3H_8][^{\bullet}NO_2]$ (10^{-7})	15	11	8.2	4.9	2.2	1.2	0.79
$k_{p-4}[C_3H_8][n\text{-}C_3H_7O^{\bullet}]$ (10^{-11})	--	6.0	5.1	4.1	4.0	4.4	5.0
$k_{p-6}[C_3H_8][i\text{-}C_3H_7O^{\bullet}]$ (10^{-10})	—	5.0	4.3	3.5	3.4	3.7	4.2

$k_{p-1}=1.6\times10^{-4}$, $k_{p-2}=1.5\times10^{-3}$, $k_{p-3}=1.6\times10^{6}$, $k_{p-4}=4.9\times10^{6}$, $k_{p-5}=1.6\times10^{6}$, $k_{p-6}=4.9\times10^{6}$ (l/mol·sec)

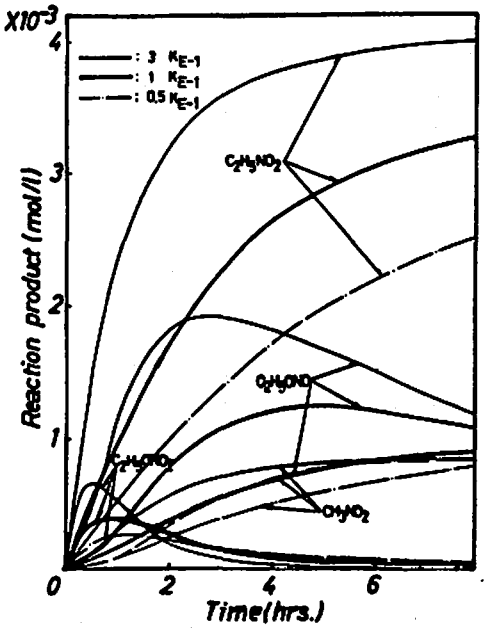


Fig. 4 Variations of concentration behavior of significant compounds with k value in the nitration of C_2H_6 with NO_2 at 185℃

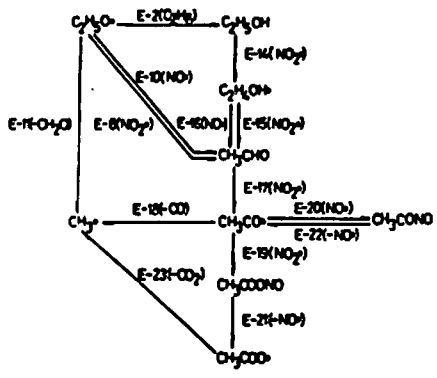
$[C_2H_6]_0$: 5×10^{-2}mol/l, $[NO_2]_0$: 2×10^{-2}mol/l

the overall reaction.

3.2.2 Paths to Main Products in Nitration of C_2H_6

$C_2H_5NO_2$ is mainly produced in reactions(E-1) and (E-4). $C_2H_5ONO_2$ and C_2H_5ONO are produced from recombination of C_2H_5O radical formed from reactions (E-1) and (E-5)with NO_2 and NO radicals, respectively (reactions (E-7)and(E-9)). These compounds subsequently decompose to give again C_2H_5O radical according to reactions (E-12) and (E-13), respectively. Consequently $C_2H_5ONO_2$ and C_2H_5ONO could behave as intermediates and their concentration behavior might depend on both the rates of their formation and decomposition. Therefore, the earlier increase of $C_2H_5ONO_2$ that C_2H_5ONO may be mainly due to the higher concentration of NO_2 radical, while the earlier decrease of the former than the latter may be due to its lower activation energy of decomposition[21].

As the fate of C_2H_5O radical, there are also some other paths as shown in Table 1. Namely CH_3 radical, CH_3CHO and C_2H_5OH are initially formed from C_2H_5O radical by its thermal decomposition (reaction (E-11)), by its disproportionation with NO_2 and NO radicals (reactions (E-8) and (E-10)) and by its hydrogen abstraction from C_2H_6 (reaction (E-2)), respectively. Then, the rates of these three reactions have been examined in order to know the relative contribution of the individual paths. Fig. 5 shows some reaction paths from C_2H_5O radical to CH_3 radical and the rates of the elementary reactions involved in these paths. As can be seen from Fig. 5, the decrease of C_2H_5O radical mostly depends ondisproportionation of C_2H_5O radical with NO_2 and NO radicals (reactions (E-8) and (E-10)). At the initial period



Rate(mol/l·sec)	Time(hrs.) 0.5	4	8	Rate(mol/l·sec)	Time(hrs.) 0.5	4	8
E-2 (10^{-11})	3.7	1.7	1.6	E-17(10^{-7})	2.2	1.1	0.55
E-6 (10^{-8})	17	2.9	0.60	E-18(10^{-11})	7.6	6.7	7.4
E-10 (10^{-8})	6.2	8.5	5.0	E-19(10^{-8})	20	5.8	1.8
E-11 (10^{-11})	11	5.8	5.5	E-20(10^{-8})	2.4	5.4	3.6
E-14 (10^{-11})	2.1	1.3	0.79	E-21(10^{-8})	10	7.3	2.2
E-15 (10^{-14})	0.62	3.0	3.9	E-22(10^{-10})	0.72	28	52
E-16 (10^{-11})	2.1	1.3	0.79	E-23(10^{-8})	10	7.3	2.2

Fig. 5 Some reaction paths from $C_2H_5O^*$ to CH_3^* and rates of elementary reactions involved in the nitration of C_2H_6 with NO_2 at 185℃

$[C_2H_6]_0 : 5\times10^{-2}$mol/l, $[NO_2]_0 : 2\times10^{-2}$mol/l

NO_2 radical and after that NO radical may mainly contribute to the above decrease of C_2H_5O radical due to its disproportionation. CH_3CHO thus produced reacts with NO_2 radical to give CH_3CO radical (reaction (E-17)). CH_3CO radical subsequently gives rise to CH_3 radical through two pathways. One of them is a direct pathway to CH_3 radical by thermal decomposition of CH_3CO radical (reaction (E-18)), and the other is a pathway through three reactions to CH_3 radical. That is, at first step CH_3CO radical reacts with NO_2 radical to give CH_3COONO (reaction (E-19)), which then decomposes to provide CH_3COO radical (reaction (E-21)) and finally (CH_3 radical is produced from subsequent decomposition of CH_3COO radical (reaction (E-23)). In this case each rate of reactions (E-19), (E-21) and (E-23) (1.8-20 x 10^{-6}, 2.2-10x10^{-6} and 2.2-10x10^{-6} mol/l·sec, respectively) is much larger than that of reaction (E-18) (6.7-7.6x10^{-11} mol/l·sec). These results suggest that CH_3 radical should be mainly produced from CH_3CO radical through reactions (E-19), (E-21) and (E-23).

CH_3 radical thus produced may then give rise to CH_3NO_2 in the reaction with NO_2 radical (reaction (E-24)). CH_3 radical may also give rise to CH_3O radical in the reaction with NO_2 radical (reaction (E-25)). Moreover CH_3O radical may provide CH_3ONO_2, CH_3ONO, CH_3OH and HCHO in the reactions of recombination with NO_2 and NO radicals (reactions (E-27) and (E-29)), hydrogen abstraction from C_2H_6 (reaction (E-3)) and disproportionation with NO_2 and NO radicals (reactions (E-28) and (E-30)), respectively. However, these products are not so significant because of the lower concentration of CH_3O radical.

3.2.3 Paths to Main Products in Nitration of C_3H_8

As discussed above, NO_2 radical is an important active species for hydrogen abstraction from C_3H_8. n-C_3H_7 and i-C_3H_7 radicals initially produced by hydrogen abstraction from C_3H_8 involving NO_2 radical (reactions (P-1) and (P-2)) react with NO_2 radical to give n-$C_3H_7NO_2$ and i-$C_3H_7NO_2$, respectively (reactions (P-7) and (P-9)). The formation ratio of n-$C_3H_7NO_2$ to i-$C_3H_7NO_2$ is about 0.12 at 159℃. This ratio, depending on the rates of the rate-determining hydrogen abstraction step involving NO_2 radical, shows that NO_2 radical may have much higher selectivity for hydrogen abstraction than alkoxyl[19)36)] and alkyl radicals[37)].

n-C_3H_7 and i-C_3H_7 radicals may also react with NO_2 radical to give n-C_3H_7O and i-C_3H_7O radicals, respectively (reactions (P-8) and (P-10)). Moreover these alkoxyl radicals may give rise to their nitrate and nitrite by recombination with NO_2 radical (reactions (P-13), (P-15), (P-17) and (P-19)), and to their carbonyl compounds such as C_2H_5CHO and CH_3COCH_3 by disproportionation with NO_2 and NO radicals (reactions (P-14), (P-18), (P-16) and (P-20)) and they may also give the corresponding alcohol compounds by their hydrogen abstraction from C_3H_8 (reactions (P-3) and (P-6)). Among these products thus formed from i-C_3H-O radical, CH_3COCH_3 is an important final product and i-$C_3H_7ONO_2$ and i-C_3H_7O NO are important intermediates, but i-C_3H_7OH is not so significant because of its lower formation rate. The products from n-C_3H_7O radical may also be not so important because of its small concentration.

4. Conclusions

The validity of the two models presented for the vapor-phase nitrations of C_2H_6 and C_3H_8 with NO_2 at lower temperatures has been examined by comparisons of the calculated and experimentally obtained concentration behavior of the significant compounds. These results showed that the above two models could elucidate almost quantitatively the behavior of the main products in our previous experiments, in spite of the fact that the nitrations are very complicated systems containing a great many elementary reactions.

In addition, some trials for quantitative interpretation on their reaction mechanism by using these models suggested that NO_2 radical should be the most important species for hydrogen abstraction from the paraffins, a significant reaction which may have a remarkable influence on the overall reactions, and that in the nitration of C_2H_6, CH_3 radical, which might react with NO_2 radical to produce CH_3NO_2, should be mainly produced from C_2H_5O radical through CH_3CHO, CH_3COONO and CH_3COO radical.

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低温での二酸化窒素によるエタンおよびプロパンの気相ニトロ化反応のモデル化

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140～200℃での二酸化窒素によるエタンおよびプロパンの気相ニトロ化反応のモデル化について検討した。反応機構に関する従来の知見を参照し，必要な素反応を選択し，最近得られた信頼し得る速度パラメータを採用して反応モデルを作成した。これら二つの反応モデルの適合性について調べた結果，これらのモデルは以前行った筆者らの実験結果をほぼ定量的に記述し得ることを示した。次いで，これらのモデルを用いて，従来不明確であった反応機構に関する定量的な解釈を試みた。その結果，ニトロ化反応にとって重要な過程であるパラフィンからの水素引抜き反応の活性攻撃種は全反応期間を通じて NO_2 であること，また，エタンのニトロ化における C_2H_5O からの CH_3 の生成はこれらの条件下では C_2H_5O からの不均化によりまず生成した CH_3CHO が，次いで CH_3COONO，CH_3COO を経る経路が主要であることが明らかとなった。

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