

in the kinetic experiments was demineralized and distilled twice in an all-quartz distillation unit. All solutions were made up by weight. The sodium hydroxide concentrations were determined (before addition of CTAB) by titration with $\text{KH}(\text{IO}_3)_2$.

Sulfonate **1f** was obtained from (*p*-chlorophenylsulfonyl) diazomethane.^{11,12a} A sample showed mp 134.5–135.0 °C; ¹H NMR (CDCl_3) δ 2.50 (2, 3 H), 4.95 (s, 2 H), 7.30–8.10 (m, 8 H). Anal. Calcd for $\text{C}_{14}\text{H}_{13}\text{ClO}_5\text{S}_2$: C, 46.60; H, 3.61. Found: C, 46.4; H, 3.6. The exact mass measured was in accord with a fragmentation leading to the loss of CH_2O from the molecular ion.³³

Kinetic Measurements. Reaction rates were determined under pseudo-first-order conditions by following the change of absorbance at 235 nm. The reactions were carried out in quartz cells placed in thermostated cell compartments of a Zeiss PMQII or a Cary Model 210 spectrophotometer. Relatively fast reactions (at higher NaOH concentration) were followed by using an Aminco-Morrow stopped-flow apparatus, equipped with a single-beam monochromator and a data acquisition storage and retrieval (DASAR) system. The optical path length of the thermostated mixing chamber was 1.0 cm. All rate constants were reproducible to within 2%. Calculations were performed by using an HP 25 programmable calculator.

Cmc Measurements. The cmc values (32.1 °C) were obtained from plots of specific conductivity ($\Omega^{-1} \text{cm}^{-1}$) vs. total CTAB concentration. A Wayne Kerr Autobalance Universal Bridge B642 fitted with a Philips electrode PW9512/01 (cell constant 0.71 cm^{-1})

was used. The following linear relations³⁴ were found:

$$\log \text{cmc} = -4.013 - 0.355 \log (\text{cmc} + [\text{NaOH}]) \quad (7)$$

$$\log \text{cmc} = -5.0966 - 0.588 \log (\text{cmc} + [\text{NaBr}]) \quad (8)$$

Equation 7 refers to the system (CTAB + NaOH) with [NaOH] ranging from 2 mM to 0.1 M. Equation 8 describes the cmc for mixtures of 5 mM NaOH, CTAB, and [NaBr] between 0 and 6 mM.

$E_T(30)$ Measurements. The $E_T(30)$ probe (2,4,6-triphenyl-*N*-[3,5-diphenyl-4-hydroxyphenyl]pyridinium betaine, kindly supplied by Prof. Ch. Reichardt, University of Marburg) dissolved in 0.1 M CTAB (25 °C) revealed $\lambda_{\text{max}} = 542 \text{ nm}$, corresponding with $E_T(30) = 52.8 \text{ kcal mol}^{-1}$. For 1,4-dioxane-water ($n_{\text{H}_2\text{O}} = 0.85$),²⁷ $E_T(30) = 54.2 \text{ kcal mol}^{-1}$.

Acknowledgment. We thank Leo A. M. Rupert for his help in the kinetic analysis.

Registry No. **1a**, 31081-12-6; **1b**, 31081-08-0; **1c**, 31081-09-1; **1d**, 14894-58-7; **1e**, 31081-11-5; **1f**, 91817-01-5; **1g**, 62586-47-4; CTAB, 57-09-0; SDS, 151-21-3; NaOH, 1310-73-2; OH^- , 14280-30-9.

Supplementary Material Available: Second-order rate constants for the reaction of **1a–g** with hydroxide ion in the presence of CTAB micelles (Table IX) and the derivation of eq 5 (4 pages). Ordering information is given on any current masthead page.

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Gas-Phase Elimination Kinetics of (Dimethylamino)alkyl Acetates. The Ion-Pair Mechanism through Neighboring Group Participation

Gabriel Chuchani,* Alexandra Rotinov, Rosa M. Domínguez, and Neil González

Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas 1010-A, Venezuela

Received February 17, 1984

The gas-phase elimination kinetics of some amino esters and a keto acetate have been studied in the temperature region of 260.0–411.5 °C and in the pressure range of 21.5–170.0 torr. These eliminations, in vessels seasoned with allyl bromide, are predominantly unimolecular and homogeneous and obey a first-order rate law. The rate coefficients for the reactions are expressible by the following Arrhenius equations: for 3-(dimethylamino)-1-propyl acetate (**1**), $\log k_1 (\text{s}^{-1}) = (12.97 \pm 0.20) - (202.1 \pm 2.5) \text{ kJ mol}^{-1} (2.303RT)^{-1}$; for 4-(dimethylamino)-1-butyl acetate (**4**), $\log k_1 (\text{s}^{-1}) = (11.91 \pm 0.43) - (163.5 \pm 4.8) \text{ kJ mol}^{-1} (2.303RT)^{-1}$; for 4-oxo-1-pentyl acetate (**7**), $\log k_1 (\text{s}^{-1}) = (12.77 \pm 0.36) - (202.8 \pm 4.6) \text{ kJ mol}^{-1} (2.303RT)^{-1}$. The presence of the $(\text{CH}_3)_2\text{N}$ group in these acetates appears to provide anchimeric assistance in the elimination; methyl acetate and the corresponding heterocyclic products arise from an intimate ion-pair mechanism. The CH_3CO substituent is believed to influence the pyrolysis rate of 5-acetoxy-2-pentanone by a weak steric acceleration.

In the past few years, our laboratory has aimed at demonstrating an intimate ion-pair-type of mechanism in the gas-phase elimination of organic molecules. Maccoll and Thomas¹ have already proposed this type of intermediate for alkyl halides and carboxylic esters pyrolyses. In this respect, we have assumed^{2,3} that such intermediates may likely occur if certain atoms within the same molecule can stabilize the reaction center in the transition state. Such a stabilization can possibly be accomplished through neighboring group participation. That is, the participation of a substituent may in some cases form an irreversible or real bond whereby an atom or group of atoms possibly

migrate or rearrange through intramolecular solvation or "autosolvation" by an intimate ion-pair mechanism. This type of intermediate appears to find support from two recent works on the gas-phase elimination of methyl esters of ω -chloro carboxylic acids³ and ethyl 4-bromobutyrate.² The formation of the corresponding lactone through rearrangement suggested that intimate ion pair mechanism by the anchimeric assistance of the COOCH_3 and $\text{COO-CH}_2\text{CH}_3$ substituents.

No homogeneous gas-phase study of rearrangement in ester pyrolysis has been reported, aside from a single case of rate enhancement in $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OAc}$ through neighboring group participation of the CH_3S group.⁴ Therefore, the present work is addressed to study the

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Table I. Distribution of Ketopentenes from Pyrolysis of 7 at Different Residence Time and Temperature

temp, °C	reaction, %	residence time, min	yield, %	
			8	9
380.3	26	13	83.0	17.0
411.6	26	3	84.5	15.5
380.3	40	23	44.2	55.8
411.6	40	5	70.0	30.0
380.3	60	40	32.3	67.7
411.6	60	8	55.1	44.9

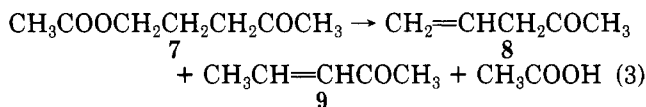
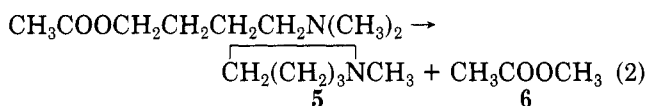
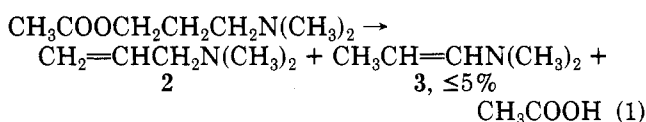
Table II. Variation of Ketopentene Formation from Pyrolysis Percentage of 7 at 411.6 °C

keto acetate decomp, %	time, min	8, %	9, %	8/9
26	3	84.5	15.5	5.5
40	5	70.0	30.0	2.3
50	7	57.9	42.1	1.4
60	8	55.1	44.9	1.2
70	10	38.7	61.3	0.6

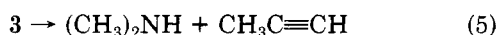
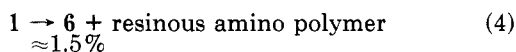
kinetics of elimination of the (dimethylamino)alkyl acetate series in the gas phase. This endeavor arises from the fact that the $(\text{CH}_3)_2\text{N}$ is a highly polarizable substituent⁵ capable of participating in the stabilization of the reaction center within the same molecule. In addition to this fact, the gas-phase pyrolysis of 4-oxo-1-pentyl acetate will be reexamined in order to find out which factors affect the small but significant rate acceleration⁶ reported in the said compound.⁷

Results and Discussion

The products of the gas-phase elimination of 3-(dimethylamino)-1-propyl acetate (**1**), 4-(dimethylamino)-1-butyl acetate (**4**), and 4-oxo-1-pentyl acetate (**7**), in vessels seasoned with allyl bromide, are described in eq 1-3.



The stoichiometries as represented in eq 1-3 require that for long reaction time the final pressure P_f should be twice the initial pressure P_0 . A series of reaction times of 10 half-lives and four different temperatures gave an average of P_f/P_0 values of 2.57 for **1**, 1.85 for **4**, and 2.11 for **7**. The observed departure from the theoretical stoichiometry is due to the following facts: (a) A small amount of the substrate and product of reaction 1 decomposes as shown in eq 4 and 5. (b) In eq 2, under the pyrolysis condition,



5 alone was found to polymerize to a very small extent. (c) Equation 3 showed that the keto alkene products yield very

Table III. Stoichiometry of the Reaction

1 at 378.7 °C				
time, min	5	8	11	14
decomp, % (pressure)	12.4	19.7	26.3	32.7
decomp, % (GC)	13.0	18.8	24.3	31.5
4 at 300.2 °C				
time, min	6	8	10	15
decomp, % (pressure)	30.7	42.2	48.7	57.9
decomp, % (GC)	29.6	41.4	47.5	56.4
7 at 395.8 °C				
time, min	5	15	20	30
decomp, % (pressure)	20.9	50.8	65.9	77.7
decomp, % (GC)	22.5	50.9	65.2	78.9

Table IV. Homogeneity of the Reaction

S/V	$10^4 k_1, \text{s}^{-1} \text{ }^a$	$10^4 k_1, \text{s}^{-1} \text{ }^b$
1 at 368.8 °C		
1	3.28	3.30
6	3.35	3.00
4 at 300.2 °C		
1	10.81	10.24
6	23.37 ^c	10.35
7 at 400.2 °C		
1	14.5 ^c	11.20
6	52.0 ^c	11.48

^a Clean Pyrex vessel. ^b Allyl bromide seasoned. ^c Average k value.

small amounts of acetone and propylene. The distribution of the ketopentene products from the pyrolysis of **7** at different residence times and temperatures and the percentage of reaction are given in Tables I and II.

It is evident from Tables I and II that the direction of elimination for ketopentenes formation is not kinetically controlled. The greater the residence time and temperature of pyrolysis (Table I), the higher the formation of the conjugated keto alkene. Similarly, at a greater percentage decomposition of the said acetate (Table II), there is an increase of the conjugated ketopentene product. These results arise by the isomerization of **8** in the presence of acetic acid under similar conditions of pyrolysis. As the reaction process increases, the concentration of acetic acid product also increases which is responsible for the isomerization of the terminal keto alkene to the conjugated keto alkene.

Confirmation of the stoichiometries, for eq 1 up to 40% decomposition, for eq 2 up to 60% decomposition, and for eq 3 up to 80% decomposition, was possible by comparing the percentage decomposition from pressure measurements with those obtained from the chromatographic analyses of the reacted amount of ester substrate (Table III).

The reactions were examined for homogeneity by using a vessel packed with glass tubing in which the surface-to-volume ratio has been increased by a factor of 6 compared with the unpacked vessel (Table IV). The clean and seasoned, packed and unpacked Pyrex vessels had no surface effect on **1**. However, the packed, clean Pyrex vessel shows an appreciable effect on the rate of elimination of **4**, while packing and unpacking has no significant effect on the rate coefficients of **7**, if the vessels are seasoned with allyl bromide.

The presence of different proportions of the free radical inhibitor propene showed no effect on the rate coefficients of these esters (Table V). No induction period was observed.

The first-order rate coefficients of the substrates calculated from $k_1 = 2.303t \log P_0/(2P_0 - P_f)$ has been found to be independent of the initial pressure. The plot of log

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Table V. Effect of Propene Inhibitor on Rates

P_0 , torr	P_i , torr	P_i/P_0	$10^4 k_1$, s ⁻¹
1 at 368.8 °C			
180			3.28
107.5	63.5	0.59	3.41
112	91.5	0.82	3.23
90.5	166.0	1.83	3.28
4 at 309.6 °C			
91.5			17.13
72.0	32.0	0.44	17.28
70.5	79.5	1.13	17.11
66	189	2.86	17.47
7 at 400.2 °C			
82			11.36
94	54.5	0.58	10.90
73.5	77.0	1.05	11.16
67.5	140.5	2.08	11.18

($2P_0 - P_i$) against time t gave a straight line up to 40% decomposition for 1, up to 60% decomposition for 4, and up to 80% decomposition for 7. The variation of the rates of elimination with temperature (Table VI) gives, by the least-squares procedure and 0.8 confidence coefficient, the following Arrhenius equations.

$$1: \log k_1 (\text{s}^{-1}) = [(12.97 \pm 0.20) - (202.1 \pm 2.5) \text{ kJ/mol}]/(2.303RT)$$

$$r = 0.9998$$

$$4: \log k_1 (\text{s}^{-1}) = [(11.91 \pm 0.43) - (163.5 \pm 4.8) \text{ kJ/mol}]/(2.303RT)$$

$$r = 0.9990$$

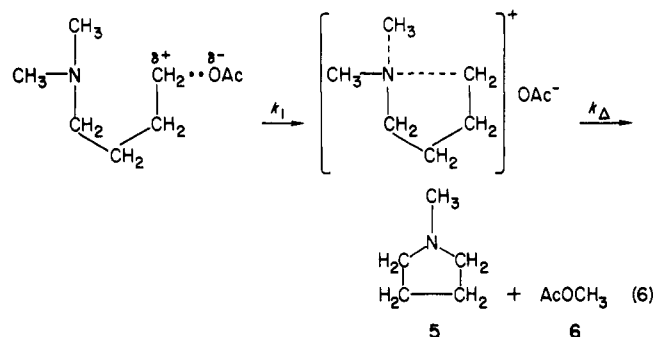
$$7: k_1 (\text{s}^{-1}) = [(12.77 \pm 0.36) - (202.8 \pm 4.6) \text{ kJ/mol}]/(2.303RT)$$

$$r = 0.9994$$

Examination of the kinetic data described in Table VII reveals that the dimethylamino substituent at the alcoholic side of acetates affects the elimination rates in various ways. First, when the $(\text{CH}_3)_2\text{N}$ group is at the β -carbon atom as in 2-(dimethylamino)ethyl acetate, its influence slows down the pyrolysis rate. This fact has already been explained in a recent paper,⁴ where it was reported that polar β -substituents in acetates tend to decrease the rate of AcOH elimination. That is, the greater the electron-withdrawing nature of the polar group the slower the py-

rolysis. In this sense, these groups gave good linear relationships by plotting $\log k/k_0$ vs. σ values ($\rho^* = -0.19$, $r = 0.961$ at 400 °C) and $\log k/k_0$ against σ_1 ($\rho_1 = -1.03$, $r = 0.960$ at 400 °C).

The influence of the $(\text{CH}_3)_2\text{N}$ group at the γ -carbon atom in 1 is difficult to assess, but prior to any reasonable interpretation in this respect, it seems convenient to analyze the results for the substrate 4, 1-butyl acetate. The higher rate of this amino ester with respect to the corresponding unsubstituted acetate (Table VII) together with the formation of 5 and 6 (eq 2) suggests that the $(\text{CH}_3)_2\text{N}$ is providing an anchimeric assistance in the stabilization and polarization of the $\text{C}_\alpha\text{-O}$ bond in the transition state. Consequently, the reaction mechanism may be explained in terms of an intimate ion-pair-type of intermediate (eq 6), where the acetoxy ion proceeds by an intramolecular



solvation or "autosolvation" to form 5 and 6 on elimination.

The above results render the question of what would be the most plausible effect of the $(\text{CH}_3)_2\text{N}$ in the pyrolysis of 1.

A recent paper⁶ has shown that alkyl groups and several polar substituents interposed by at least a methylene group at the β -carbon atom of acetates, i.e., $\text{ZCH}_2\text{CH}_2\text{OAc}$, enhanced the rate of the reaction due to steric acceleration. Thus, plotting $\log k/k_0$ against Hancock steric parameters E_s^c values gave a good straight line ($\delta = -0.121$, $r = 0.935$ at 400 °C). In considering the E_s^c value of the $(\text{CH}_3)_2\text{NCH}_2$ substituent this steric parameter has not been reported, but is must evidently be lower than the $(\text{CH}_3)_2\text{CHCH}_2$ substituent ($E_s^c = -2.48$). If a relatively smaller E_s^c value for the $(\text{CH}_3)_2\text{NCH}_2$ is assumed, the plotting position is way above the slope of the line when projected in the Hancock correlation for $\text{ZCH}_2\text{CH}_2\text{OAc}$ pyrolysis.⁶ Oth-

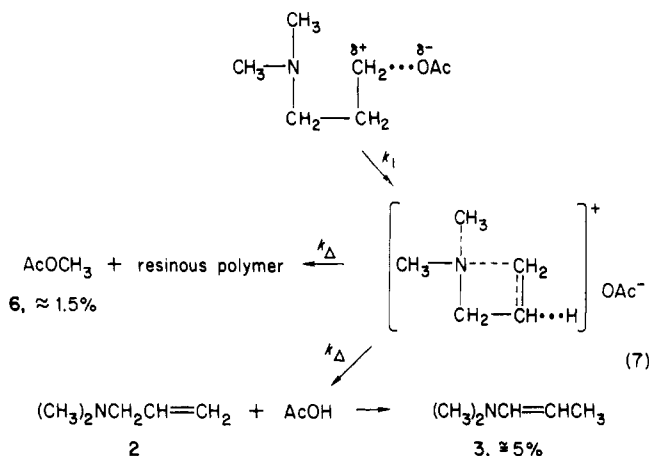
Table VI. Temperature Dependence of Rate Coefficients

	1							
T , °C	347.1	357.3	363.5	368.8	375.2	378.7	387.9	392.7
$10^4 k_1$, s ⁻¹	0.91	1.63	2.49	3.30	4.78	5.80	9.75	13.24
	4							
T , °C	260.0	270.7	279.9	290.4	300.2	309.6	319.6	
$10^4 k_1$, s ⁻¹	0.74	1.72	3.12	5.68	10.24	17.29	31.62	
	7							
T , °C	380.4	385.6	391.4	395.8	400.2	405.5	411.5	
$10^4 k_1$, s ⁻¹	3.70	4.90	6.52	8.80	11.20	14.41	19.90	

Table VII. Kinetic Parameters at 400 °C

acetate	$10^4 k_1$, s ⁻¹	$10^4 k_H$, s ⁻¹	rel rate per H	E_a , kJ/mol	$\log A$, s ⁻¹	ref
ethyl	10.00	3.33	1.0	200.4 (± 3.8)	12.55 (± 0.30)	7
$\text{CH}_3\text{COCH}_2\text{CH}_2\text{NMe}_2$	6.17	3.09	0.9	220.4 (± 3.8)	13.90 (± 0.30)	4
<i>n</i> -Pr	8.51	4.26	1.0	204.1 (± 3.8)	12.77 (± 0.30)	7
1	19.50	9.75	2.3	202.1 (± 2.5)	12.97 (± 0.20)	this work
<i>n</i> -Bu	10.47	5.24	1.0	199.5 (± 4.6)	12.50 (± 0.36)	7
4	1659.6	829.8	158.0	163.5 (± 4.8)	11.91 (± 0.43)	this work
7	20.14	10.07	2.4	198.9 (± 2.9)	12.74 (± 0.23)	7
7	10.72	5.36	1.3	202.8 (± 4.6)	12.77 (± 0.36)	this work

erwise, the smaller but significantly higher rate of the (dimethylamino)propyl acetate with respect to the corresponding unsubstituted propyl acetate (Table VII) appears to insinuate that the $(\text{CH}_3)_2\text{N}$ group is moderately providing anchimeric assistance in the AcOH elimination. The very low yield of **6** (eq 4) appears to support a mechanism almost similar to that described in eq 6. That is,



Even though a cyclic four-membered conformation is not very favorable for neighboring group participation, Grob and Jenny⁸ have found that 3-(dimethylamino)-1-chloropropane solvolysis has a significantly higher rate with respect to the corresponding unsubstituted alkyl chloride due to participation of the $(\text{CH}_3)_2\text{N}$ substituent.

In plotting the $\log k_{\text{rel}}$ of the ester series $\text{RCH}_2\text{CH}_2\text{OAc}$ vs. E_s^c values,⁶ the acetyl substituent ($\text{R} = \text{CH}_3\text{COCH}_2$) in the pyrolysis of **7**⁷ (Table VII) could not be defined since its point of relative rate is considerably above the slope of the line. This high rate of **7** was believed to result from difficulties in the experimental conditions or some other factors.⁶ In this sense, a kinetic redetermination of the said compound **7** shows the rate to be nearly similar with respect to the corresponding unsubstituted *n*-propyl acetate. This means, that the acetyl substituent must exert, if any, a very weak steric acceleration in the pyrolysis of 4-oxo-1-pentyl acetate (**7**). Ith the present data, the E_s^c value for the CH_3COCH_2 group can approximately be defined from the slope of the above Hancock correlation as -1.88 .

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Experimental Section

3-(Dimethylamino)-1-propyl Acetate (1). This amino ester was prepared by treating 3-(dimethylamino)-1-propanol (Aldrich) with acetic anhydride as described⁹ (bp 108–110 °C (72 torr); lit.¹⁰ bp 163–167 °C (750 torr)). The acetate was distilled to 99.7% purity as determined by GLC (Carbowax 20 M, 0.30% KOH, 80–100 mesh). Allyldimethylamine, dimethylpropenylamine, and propyne were unequivocally identified by mass spectrometry analysis. These reaction products together with methyl acetate (Baker) and dimethylamine (Matheson) were analyzed in the same Carbowax column. 1-Methylazacyclobutane is apparently unstable under the pyrolysis condition and polymerizes readily before any possible analysis.

4-(Dimethylamino)-1-butyl Acetate (4). 4-Bromobutyl acetate (Aldrich) was treated with dimethylamine (Matheson) as described.¹¹ The product had a boiling point of 83 °C at 9 torr (lit. bp 89–90 °C at 12 torr¹¹). It was fractionated several times and the fraction of 98.7% purity as determined by GLC (28% Pennwalt 223 + 4% KOH-Gas-Chromosorb R 80-100 mesh) was used. *N*-Methylpyrrolidine (Aldrich) and methyl acetate (Baker) were analyzed with the same column.

4-Oxo-1-pentyl Acetate (7). Treatment of 5-hydroxy-2-pentanone (K & K Labs) with acetic anhydride in pyridine yielded the corresponding acetate. Several distillations of the product gave a boiling point at 99 °C (14 torr) [lit.¹² bp 91 °C (12 torr)] and a purity of 99.2% when analyzed by GLC (FFAP 7%, Chromosorb W AW DMCS, 80–100 mesh). 4-Penten-2-one was prepared by passing 5-chloro-2-pentanone over soda lime, and 3-penten-2-one by isomerization of 4-penten-2-one with HCl in the gas phase. These keto alkenes were identified by NMR and mass spectrometry analysis.

Kinetics. The experiments were carried out in a static system¹³ with the vessels seasoned by the product of allyl bromide decomposition.¹³ The kinetic measurements were determined by the unreacted amount of the substrate as determined by GLC and/or by pressure increase. The starting materials were injected directly into the reaction vessel with a syringe through a silicon rubber septum, the temperature being maintained to better than ± 0.2 °C calibrated with an iron constantan.

Acknowledgment. This work was generously supported by the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT) under Project No. 51.78.31; S1-1072.

Registry No. 1, 4339-94-0; 4, 2948-10-9; 7, 5185-97-7.

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