Kinetics of Copper(II)-Catalyzed Cyclopropanation of Olefins

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Abstract—Kinetics of the copper(II) acetylacetonate–catalyzed cyclopropanation of styrene and 2,5-dimethylhexa-2,4-diene is reported. A kinetic analysis of a catalytic olefin cyclopropanation scheme is suggested.

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The catalytic dediazotization of alkyl diazoacetates in the presence of olefins yields derivatives of cyclopropanoic acid. Efficient catalysts for this reaction under both heterogeneous and homogeneous conditions are copper salts [1–3]. Here, we report the cyclopropanation of styrene and 2,5-dimethylhexa-2,4-diene in the presence of copper acetylacetonate $Cu(acac)_2$. Based on the experimental data, we perform a kinetic analysis of the cyclopropanation reaction scheme.

EXPERIMENTAL

Methyl and ethyl diazoacetates—$CH_3OC(O)CHN_2$ and $C_2H_5OC(O)CHN_2$—were synthesized using a procedure described in [4]. Styrene ($PhCH=CH_2$) was washed with an aqueous solution of potassium hydroxide to remove the stabilizer (hydroquinone), dried over calcined calcium chloride, distilled at a reduced pressure (~20 Torr), again dried over calcium chloride, and redistilled. Copper acetylacetonate, $Cu(acac)_2$, was synthesized as described in [5]. Copper trifluoromethanesulfonate ($Cu(OTf)_2$, 98%) and 2,5-dimethylhexa-2,4-diene (($CH_3)_2C=CHCH=C(CH_3)_2$, 96%), both from Aldrich, were used as received. Dichloroethane was held over sodium hydroxide, refluxed over P_2O_5 in an inert atmosphere, and distilled from P_2O_5 [6].

The yields of the methyl and ethyl esters of 2-phenylcyclopropanecarboxylic acid present in the reaction mixture were quantified by GLC (plasma ionization detector, 200×0.3 cm column packed with 10% Carbowax 20M on Inerton AW, helium as the carrier gas, dibutylsulfone as the internal standard). Methyl and ethyl 2-phenylcyclopropanecarboxylates were isolated chromatographically (24×1 cm column packed with SiO_2-60 (Merck), hexane/ethyl acetate = 15 : 1). ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AMX 300 spectrometer operating at 300.13 and 75.75 MHz, respectively, using $CDCl_3$ as the solvent.

Kinetic measurements were carried out using a manometric setup [7]. The catalyst was placed in a temperature controlled reactor, the reactor was vacuumized, and the apparatus was filled with nitrogen gas. Next, an olefin, a diazo compound, and water were introduced successively into the reactor. Cyclopropanation kinetics was monitored as the nitrogen evolution rate.

Spectrophotometric experiments were carried out on a Specord UV-VIS spectrometer and an SF-26 spectrophotometer. A catalyst and dichloroethane were placed in a quartz cell with an optical path length of 1 cm, and the cell was sealed and was purged for 15 min with argon or nitrogen. Next, 2,5-dimethylhexa-2,4-diene, methyl diazoacetate, and water were introduced successively into the cell and the time evolution of the absorbance of the reaction mixture was recorded at room temperature. The reaction rate was determined from the variation of absorbance at a wavelength of $\lambda = 630$ nm.

RESULTS AND DISCUSSION

The catalytic decomposition of the diazo compound $ROC(O)CHN_2$ in the presence of styrene or 2,5-dimethylhexa-2,4-diene was studied at 296 K in a dichloroethane solution. The initial reactant concentrations were varied in the following ranges (mol/l): $[CH_3OC(O)CHN_2] = 0.07–4.9$, $[C_2H_5OC(O)CHN_2] = 0.2–1.0$, $[PhCH=CH_2] = 0–8$, $[(CH_3)_2C=CHCH=C(CH_3)_2] = 0–5.8$, $[Cu(OTf)_2] = (0.9–5.7) \times 10^{-2}$, $[Cu(acac)_2] = (0.7–3.6) \times 10^{-2}$, and $[H_2O] = 0.2–0.5$.
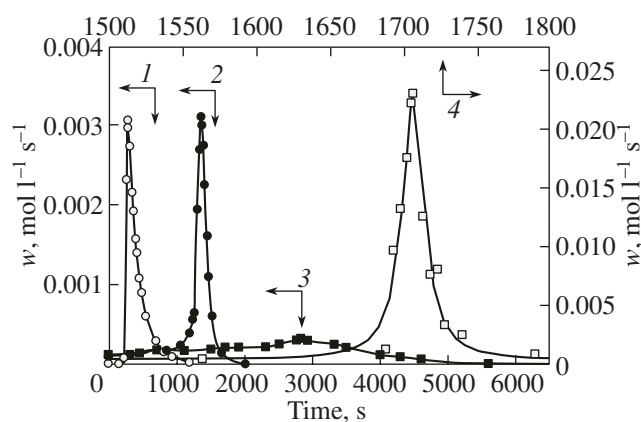
Fig. 1. Time variation of the nitrogen evolution rate in the catalytic decomposition of methyl diazoacetate in the presence of an olefin at 296 K: (*1*) [PhCH=CH$_2$] = 1.5 mol/l, [Cu(OTf)$_2$] = 1.3 × 10^{-2} mol/l, and [C$_2$H$_5$OC(O)CHN$_2$] = 1 mol/l; (*2*) [(CH$_3$)$_2$C=CHCH=C(CH$_3$)$_2$] = 1.2 mol/l, [Cu(acac)$_2$] = 1.9 × 10^{-2} mol/l, [CH$_3$OC(O)CHN$_2$] = 0.9 mol/l, and [H$_2$O] = 0.5 mol/l; (*3*) [PhCH=CH$_2$] = 2.2 mol/l, [Cu(acac)$_2$] = 2.1 × 10^{-2} mol/l, [CH$_3$OC(O)CHN$_2$] = 0.9 mol/l, and [H$_2$O] = 0.5 mol/l; (*4*) no olefin, [Cu(acac)$_2$] = 1.8 × 10^{-2} mol/l, [CH$_3$OC(O)CHN$_2$] = 0.9 mol/l, and [H$_2$O] = 0.5 mol/l.

Kinetics of the Process

The gas evolution rate w passed through an extremum during the reaction: after an induction period, w increased up to its maximum value w_{max} and then fell off almost to zero (Fig. 1). In the absence of an olefin, the induction period was somewhat longer and the maximum gas evolution rate was higher (Fig. 1). As the styrene or 2,5-dimethylhexa-2,4-diene concentration was
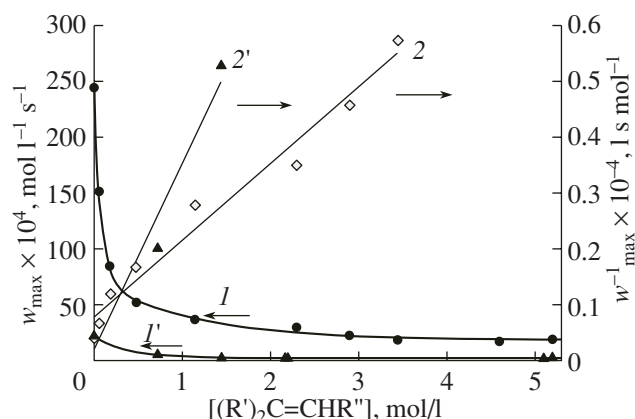
raised, w_{max} decreased to become constant within the experimental error at an olefin concentration above 1.5 mol/l (Tables 1, 2, Fig. 2).

It follows from our experimental data that w_{max} increases linearly with increasing catalyst concentration (Table 1), while the dependence of w_{max} on the diazo compound concentration is nonlinear (Fig. 3). As can be seen from Fig. 3, the effective order of the reaction (n_{eff}) with respect to the diazo compound concentration increases with increasing [ROC(O)CHN$_2$] and lies between 2 and 3. In earlier studies [3, 8, 9], it was found that the reaction is first-order with respect to the diazo compound concentration; note, however, that those studies were performed in a narrow range of diazo compound concentrations (usually 0–0.3 mol/l).

As the temperature is raised, w_{max} increases as follows ([Cu(acac)$_2$] = 7 × 10^{-3} mol/l, [CH$_3$OC(O)CHN$_2$] = 1 mol/l, [PhCH=CH$_2$] = 8 mol/l):

T, K	289	296	305	324
$w_{max} \times 10^5$, mol l^{-1} s^{-1}	3.5	15.3	47.0	136.0

As can be seen from Tables 1 and 3, the maximum gas evolution rate is one order of magnitude higher in styrene cyclopropanation catalyzed by copper trifluoromethanesulfonate than in the same reaction catalyzed by copper acetylacetonate. A comparison between the reactivities of styrene and 2,5-dimethylhexa-2,4-diene in cyclopropanation under the same conditions (with copper acetylacetonate as the catalyst; see Tables 1 and 2) demonstrated that w_{max} for the latter compound is higher by a factor of 6. The higher reactivity of copper trifluoromethanesulfonate as compared to copper
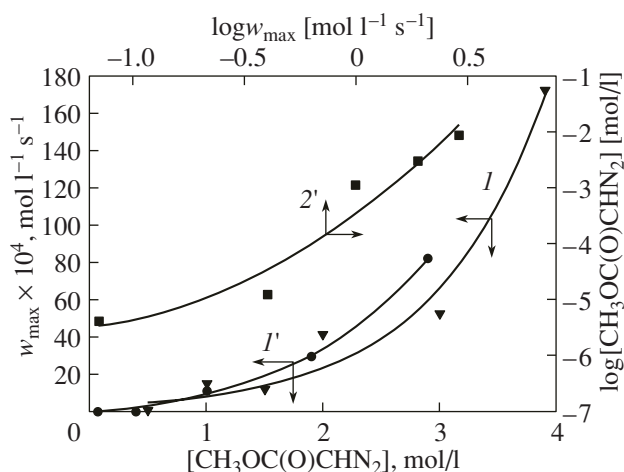

Fig. 2. Plots of w_{max} versus the (*1*) 2,5-dimethylhexa-2,4-diene and (*1'*) styrene concentrations and (*2, 2'*) the anamorphoses of this plots in the coordinates of Eq. (5). [CH$_3$OC(O)CHN$_2$] = 1 mol/l, [Cu(acac)$_2$] = (*1*) 1.8 × 10^{-2} and (*1'*) 0.7 × 10^{-2} mol/l, [H$_2$O] = 0.5 mol/l, and T = 296 K.

Fig. 3. Plots of w_{max} versus the methyl diazoacetate concentration for methyl diazoacetate decomposition in the presence of (*1*) 2,5-dimethylhexa-2,4-diene and (*1'*) styrene. (*2'*) Anamorphosis of curve *1'* in logarithmic coordinates. [PhCH=CH$_2$] = 1.5 mol/l, [(CH$_3$)$_2$C=CHCH=C(CH$_3$)$_2$] = 2.3 mol/l, [Cu(acac)$_2$] = (*1*) 1.8 × 10^{-2} and (*1'*) 3.6 × 10^{-2} mol/l, [H$_2$O] = 0.5 mol/l, and T = 296 K.

acetylacetonate in the reaction involving styrene is a known fact; however, it is difficult to explain the dependence of w_{max} on the olefin structure (e.g., on a simple increase in the number of double bonds). Since the alkoxycarbonylcarbene ROC(O)CH:, which results from the decomposition of the diazo compound and plays the key role in the reaction, shows electrophilic properties [1], we assumed that the difference between its reactivities toward the olefins examined is due to these olefins having different ionization potentials. Indeed, the ionization potential of styrene is 8.43 eV and that of 2,5-dimethylhexa-2,4-diene has a much smaller value of 7.67 eV [10].

Table 4 presents the results of an experiment in which cyclopropanation was performed in several steps. In this experiment, after gas evolution from the initial reaction mixture was complete, we added another portion of the diazo compound to the remaining mixture of styrene and the catalyst in dichloroethane, ruling out air access into the reactor. Immediately after the introduction of a fresh portion of $CH_3OC(O)CHN_2$, the gas evolution rate reached the highest possible value under the given conditions, so there was no induction period (Fig. 4). This is evidence that the operating catalyst retains its activity in a sealed system for a long time.

Generation of Active Sites

Copper(I) compounds are known to be more efficient cyclopropanation catalysts than copper(II) compounds [3]. For this reason, we studied the kinetics of Cu(II) conversion into Cu(I) in the reaction mixture. The 2,5-dimethylhexa-2,4-diene–methyl diazoacetate–$Cu(acac)_2$ system at room temperature was used as the model. The optical absorption spectrum of copper(II) acetylacetonate dissolved in dichloroethane shows a peak in the wavelength range of 500–650 nm (Fig. 5).

The addition of 2,5-dimethylhexa-2,4-diene to a mixture of $Cu(acac)_2$ and dichloroethane exerts no effect on the spectrum. After the addition of methyl diazoacetate, absorbance at $\lambda < 500$ nm increases with time and absorbance at $\lambda > 530$ nm decreases with time. The kinetics of Cu(II) conversion into Cu(I) was traced as absorbance at 630 nm by recording the absorption spectra of the reaction mixture at certain intervals, beginning immediately after the addition of methyl diazoacetate to the mixture of $Cu(acac)_2$ and 2,5-dimethyl-hexa-2,4-diene in dichloroethane (Fig. 5). Note that the time interval between the introduction of the diazo compound into the reaction mixture and the maximum gas evolution rate (w_{max}) point (induction period) is close to the time taken by the absorbance of the reaction mixture ($\lambda > 500$ nm) to fall to zero. This time in the case considered is about 60 min. It can be assumed that the induction period is related to $Cu(acac)_2$ conversion into a more active species containing Cu(I). This assumption is supported by the fact that the reaction mixture changes from grayish blue to greenish during

Table 1. w_{max} data as a function of the styrene, copper(II) acetylacetonate, and methyl diazoacetate concentrations

$[Cu(acac)_2] \times 10^2$, mol/l	$[CH_3OC(O)CHN_2]$, mol/l	$[PhCH=CH_2]$, mol/l	$w_{max} \times 10^4$, mol l^{-1} s^{-1}
0.7	1.0	0	21.4
	1.0	0.7	5.0
	1.0	1.5	1.9
	1.0	2.2	2.5
	1.0	5.1	1.5
	1.0	5.2	2.1
	1.0	6.5	1.5
	1.0	8.0	1.7
	1.0	5.1	2.0
	2.9	5.1	3.8
	4.9	5.1	5.7
1.0	1.0	5.1	3.0
1.2	1.0	5.1	2.6
2.3	1.0	5.1	6.8
3.4	1.0	5.1	10.7
3.6	0.07	1.5	0.04
	0.4	1.5	0.12
	1.0	1.5	10.7
	1.9	1.5	29.2
	2.9	1.5	81.3

Note: $[H_2O] = 0.5$ mol/l and $T = 296$ K.

the induction period. If, after absolute transparence at $\lambda > 500$ nm is reached, the cell is opened in air, the absorbance of the solution will increase nearly to its initial value. This is evidence that Cu(I)) is oxidized with atmospheric oxygen to Cu(II).

These results and an analysis of the literature [3, 8, 9, 11–13] suggest that the catalyst is activated during the induction period. Figure 6 shows kinetic traces of the $Cu(acac)_2$ concentration and the anomorphoses of these traces in the first-order equation coordinates.

Analysis of the Styrene Cyclopropanation Products

It was found by GLC that, under our experimental conditions ($[CH_3OC(O)CHN_2] = 1$ mol/l, $[Cu(acac)_2] = 7 \times 10^{-3}$ mol/l, $T = 296$ K) at $[PhCH=CH_2]/[CH_3OC(O)CHN_2] \approx 5 : 1$, 2-phenylcy-clopropanecarboxylic acid methyl ester (PCPCAME) forms in nearly quantitative yield in terms of the initial amount of methyl diazoacetate (Table 5). The *trans*/*cis*

Table 2. w_{max} data as a function of the 2,5-dimethylhexa-2,4-diene and methyl diazoacetate concentrations

[CH₃OC(O)CHN₂], mol/l	[(CH₃)₂C=CHCH=C(CH₃)₂], mol/l	$w_{max} \times 10^4$, mol l⁻¹ s⁻¹
1.0	0	244.1
	0.06	150.8
	0.2	83.8
	0.4	43.5
	0.6	60.3
	1.2	36.2
	2.3	28.6
	2.9	21.9
	3.5	17.5
	4.6	16.1
	5.2	17.8
	5.8	24.7
	5.8	16.8
0.2	0.6	0.3
0.5	2.3	0.8
1.0	2.3	14.9
1.5	2.3	11.5
2.0	2.3	41.0
3.0	2.3	52.0
3.9	2.3	171.5

Note: [Cu(acac)₂] = 1.8×10^{-2} mol/l, [H₂O] = 0.5 mol/l, and T = 296 K.

Table 3. Maximum gas evolution rate data for styrene cyclopropanation in the presence of copper trifluoromethanesulfonate

[Cu(OTf)₂] × 10², mol/l	[C₂H₅OC(O)CHN₂], mol/l	$w_{max} \times 10^4$, mol l⁻¹ s⁻¹
2.3	0.2	0.1
3.5	0.2	0.3
4.5	0.2	0.2
5.7	0.2	0.2
0.9	1.0	29.0
1.4	1.0	34.1

Note: [PhCH=CH₂] = 1.5 mol/l, [H₂O] = 0.5 mol/l, and T = 296 K.

isomer ratio is ~3/2 and is almost independent of the reaction conditions. This isomer ratio is typical of styrene cyclopropanation catalyzed by copper(II) compounds [14–18].
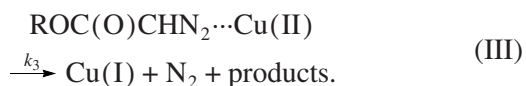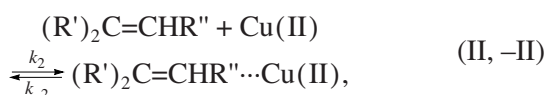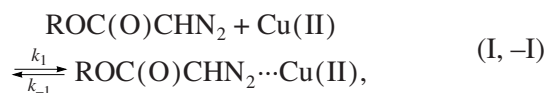
The [PhCH=CH₂]/[CH₃OC(O)CHN₂] ratio has an effect on the PCPCAME yield (Y) and PCPCAME selectivity (S). These values were determined as $Y = (n_{PCPCAME}/n_{MDA}) \times 100$ and $S = (n_{PCPCAME}/\Delta n_{MDA}) \times 100$, where $n_{PCPCAME}$ is the number of moles of the resulting PCPCAME, n_{MDA} is the initial number of moles of methyl diazoacetate, and Δn_{MDA} is the number of methyl diazoacetate moles consumed (Table 5). In the selectivity calculations, we took into account that the amount of nitrogen evolved (n_{N_2}) is equal to the amount of decomposed methyl diazoacetate (Δn_{MDA}).

The main product of the reaction between styrene and ethyl diazoacetate in the presence of copper trifluoromethanesulfonate is phenylcyclopropanecarboxylic acid ethyl ester. Its yield in terms of ethyl diazoacetate consumed is nearly quantitative (Table 5).

As calculated from the dediazotization rate, the molar amount of nitrogen evolved is no less than 80% of the molar amount of the diazo compound decomposed.

Kinetic Scheme of the Process

The observed kinetics and earlier reported data known to us [3, 8, 9, 11–13, 19] can be accounted for by the following cyclopropanation scheme:
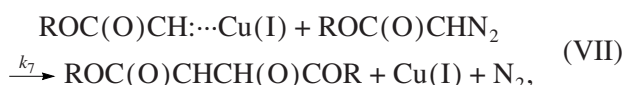
$$\text{ROC(O)CHN}_2 + \text{Cu(II)} \quad\quad\quad\quad \text{(I, –I)}$$
$$\xrightleftharpoons[k_{-1}]{k_1} \text{ROC(O)CHN}_2\cdots\text{Cu(II)},$$

$$(\text{R'})_2\text{C=CHR''} + \text{Cu(II)} \quad\quad \text{(II, –II)}$$
$$\xrightleftharpoons[k_{-2}]{k_2} (\text{R'})_2\text{C=CHR''}\cdots\text{Cu(II)},$$

$$\text{ROC(O)CHN}_2\cdots\text{Cu(II)} \quad\quad\quad \text{(III)}$$
$$\xrightarrow{k_3} \text{Cu(I)} + \text{N}_2 + \text{products}.$$

Catalytic cycle:

$$\text{ROC(O)CHN}_2 + \text{Cu(I)} \quad\quad\quad \text{(IV, –IV)}$$
$$\xrightleftharpoons[k_{-4}]{k_4} \text{ROC(O)CHN}_2\cdots\text{Cu(I)},$$

$$(\text{R'})_2\text{C=CHR''} + \text{Cu(I)} \quad\quad \text{(V, –V)}$$
$$\xrightleftharpoons[k_{-5}]{k_5} (\text{R'})_2\text{C=CHR''}\cdots\text{Cu(I)},$$

$$\text{ROC(O)CHN}_2\cdots\text{Cu(I)} \quad\quad\quad \text{(VI)}$$
$$\xrightarrow{k_6} \text{ROC(O)CH:}\cdots\text{Cu(I)} + \text{N}_2,$$

$$\text{ROC(O)CH:}\cdots\text{Cu(I)} + \text{ROC(O)CHN}_2 \quad \text{(VII)}$$
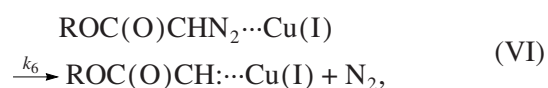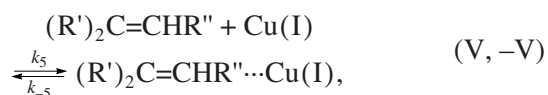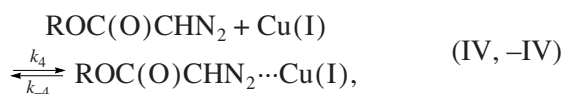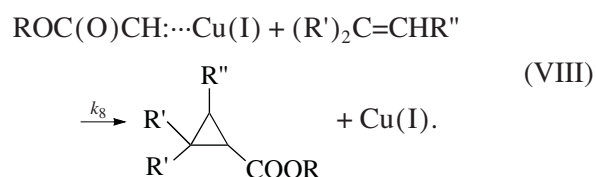$$\xrightarrow{k_7} \text{ROC(O)CHCH(O)COR} + \text{Cu(I)} + \text{N}_2,$$

Table 4. Changes in the nitrogen evolution rate (w_{max}) upon the portionwise addition of methyl diazoacetate to the reaction mixture

V_{MDA}, ml	$[CH_3OC(O)CHN_2]$, mol/l	$[PhCH=CH_2]$, mol/l	$w_{max} \times 10^5$, mol l^{-1} s^{-1}	n_{N_2}, mmol	n_{MDA}, mmol	Y, mol %	V_r, ml
0.2	0.18	5.3	1.2	0.7	1.2	–	6.6
0.2	0.34	5.1	6.9	2.2	2.3	19	6.8
0.1	0.22	5.0	3.5	1.1	1.3	88	6.0
0.1	0.21	4.9	3.6	1.1	1.2	86	5.7

Note: $[Cu(acac)_2] = 8 \times 10^{-3}$ mol/l, $[H_2O] = 0.2$ mol/l, and $T = 296$ K. V_{MDA} is the volume of methyl diazoacetate added, n_{MDA} is the number of moles of the initial methyl diazoacetate, n_{N_2} is the molar amount of nitrogen evolved, Y is the PCPCAME yield in terms of methyl diazoacetate introduced in the reaction, and V_r is the volume of the reaction mixture (the decrease in V_r is due to sampling for GLC).

$$ROC(O)CH:\cdots Cu(I) + (R')_2C=CHR''$$

(VIII)

$$\xrightarrow{k_8} \begin{matrix} R'' \\ R' \\ R' \quad COOR \end{matrix} + Cu(I).$$

Loss of active sites:

$$Cu(I) \xrightarrow{k_9} \text{nonreactive products.} \qquad (IX)$$

In this scheme, Cu(I) and Cu(II) stand for catalytic complexes containing univalent and divalent copper, $R = CH_3$ or C_2H_5, $R' = CH_3$ or H, and $R'' = (CH_3)_2C=CH$ or Ph.

It is likely that the scheme is also applicable to the reaction involving 2,5-dimethylhexa-2,4-diene since

this compound is known to be mainly cyclopropanated at one of its double bonds [20–22]. The scheme assumes that the active form of the catalyst is a copper(I) complex. The main product results from the interaction between the metal carbene complex $[ROC(O)CH:\cdots Cu(I)]$ and the olefin (reaction step (VIII)).

According to the kinetic scheme, the olefin cyclopropanation reaction shows all the basic features of chain processes. Therefore, it can be analyzed using known means of describing nonbranched chain reactions. In particular, in view of the low catalyst concentration, it can be stated that the "chain length" (i.e., the number of catalytic cycles per active site) is large and the long chain condition is applicable here, according
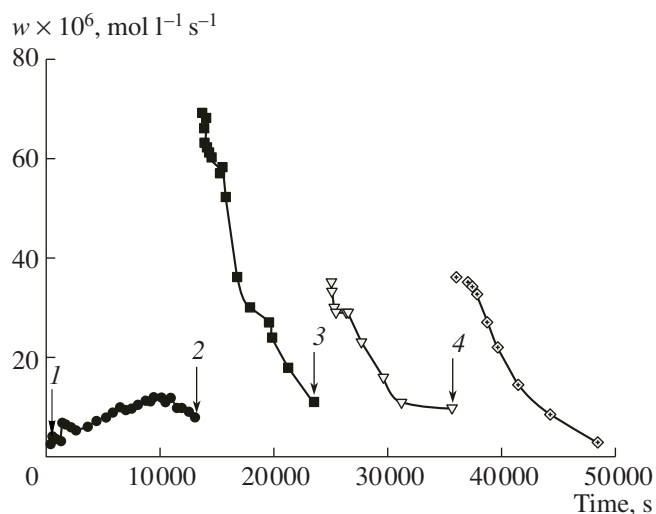

Fig. 4. Time variation of the gas evolution rate in the catalytic decomposition of methyl diazoacetate in the styrene medium under conditions of portionwise addition of $CH_3OC(O)CHN_2$. The arrows indicate the points of time at which methyl diazoacetate aliquots (ml) are added: (1) 0.2, (2) 0.2, (3) 0.1, and (4) 0.1. $[PhCH=CH_2] = 5.3$ mol/l, $[Cu(acac)_2] = 8 \times 10^{-3}$ mol/l, and $[H_2O] = 0.2$ mol/l. $T = 296$ K.
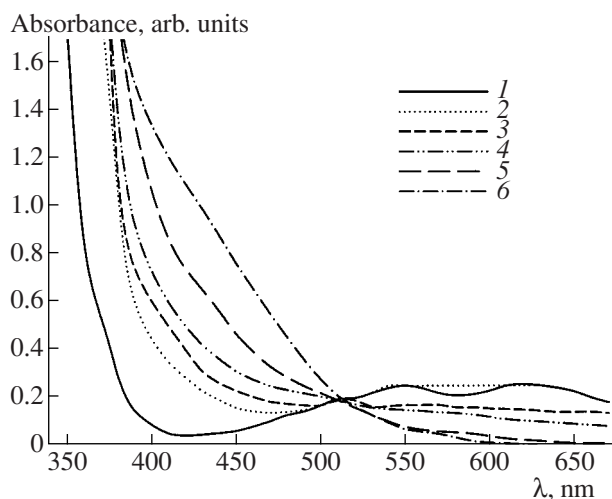

Fig. 5. Optical absorption spectra of a reacting mixture of 2,5-dimethylhexa-2,4-diene and copper acetylacetonate in dichloroethane (1) in the absence of methyl diazoacetate, (2) immediately after the addition of methyl diazoacetate, and (3–6) some time after the addition of methyl diazoacetate: (3) 34, (4) 41, (5) 61, and (6) 76 min. $[Cu(acac)_2] = 5.4 \times 10^{-3}$ mol/l, $[CH_3OC(O)CHN_2] = 0.7$ mol/l, $[(CH_3)_2C=CHCH=C(CH_3)_2] = 1.2$ mol/l, $[H_2O] = 0.2$ mol/l, and $T = 296$ K.
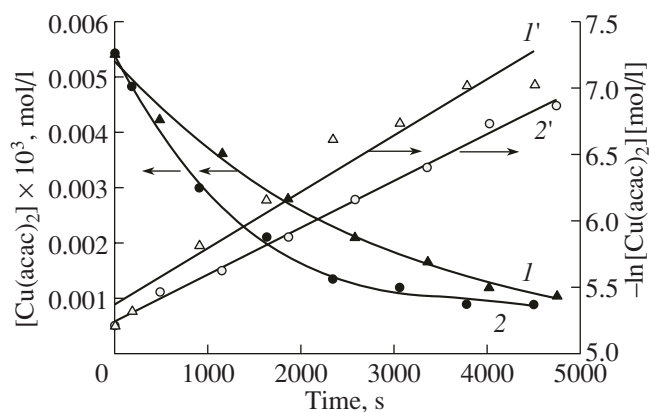
Fig. 6. Kinetic traces of Cu(acac)$_2$ consumption in (*1*) nitrogen and (*2*) argon atmospheres and (*1'*, *2'*) their semilogarithmic anamorphoses. [Cu(acac)$_2$] = 5.4 × 10^{-3} mol/l, [CH$_3$OC(O)CHN$_2$] = 0.7 mol/l, [(CH$_3$)$_2$C=CHCH=C(CH$_3$)$_2$] = 1.2 mol/l, [H$_2$O] = 0.2 mol/l, and T = 296 K.

to which the chain initiation and termination rates must be equal:

$$w_i = w_9 \text{ or } k_3[ROC(O)CHN_2 \cdots Cu(II)] = k_9[Cu(I)]. \quad (1)$$

Let us apply the ROC(O)CHN$_2$···Cu(II) quasi-stationarity condition:

$$\frac{[ROC(O)CHN_2 \cdots Cu(II)]}{dt}$$

$$= k_1[ROC(O)CHN_2][Cu(II)]$$

$$- k_{-1}[ROC(O)CHN_2 \cdots Cu(II)]$$

$$- k_3[ROC(O)CHN_2 \cdots Cu(II)] = 0.$$

Hence,

$$[ROC(O)CHN_2 \cdots Cu(II)]$$

$$= \frac{k_1[ROC(O)CHN_2][Cu(II)]}{k_{-1} + k_3}.$$

In view of this expression, equality (1) appears as

$$w_i = \frac{k_3 k_1}{k_{-1} + k_3}[ROC(O)CHN_2][Cu(II)] \quad (2)$$

$$= \alpha k_1[ROC(O)CHN_2][Cu(II)].$$

The parameter α characterizes the probability of intramolecular electron transfer in the ROC(O)CHN$_2$···Cu(II) complex, which would bring the catalyst into a more active state.

Now we will take into account that the total divalent copper concentration includes the concentration of the (R')$_2$C=CHR"···Cu(II) complex. Using the quasi-steady-state approximation, we obtain

$$K_2 = \frac{[(R')_2C=CHR'' \cdots Cu(II)]}{[Cu(II)][(R')_2C=CHR'']}$$

and

$$[Cu(II)]_\Sigma = [Cu(II)] + [(R')_2C=CHR'' \cdots Cu(II)].$$

Therefore,

$$[Cu(II)]_\Sigma = [Cu(II)] + K_2[(R')_2C=CHR''][Cu(II)]$$

$$= [Cu(II)](1 + K_2[(R')_2C = CHR'']).$$

Table 5. Effect of the concentration ratio of the starting reactants on the PCPCAME yield and selectivity

n_{MDA}, mmol	[PhCH=CH$_2$], mol/l	$\dfrac{[PhCH=CH_2]}{[CH_3OC(O)CHN_2]}$	n_{N_2}, mmol	$n_{PCPCAME}$, mmol	S, mol %	Y, mol %
			Cu(acac)$_2$			
0.7*	3.2	18	–	0.5	–	71
1.1	3.2	12	–	0.3	–	27
1.2	0	–	1.0	0	0	0
	0.73	0.75	0.7	0.3	43	25
	1.45	1.50	1.2	0.7	58	58
	2.18	2.25	1.1	0.9	82	75
	5.10	5.25	1.1	1.1	100	92
	7.98	8.23	0.9	0.7	78	58
3.6	5.10	1.75	–	2.0	–	56
			Cu(OTf)$_2$			
0.7*	3.2	18	0.6	0.6	100	86
3.8*	1.5	1.6	3.5	3.5	100	92
0.9*	8.5	37	–	0.8	–	89

Note: The catalyst concentration is 7×10^{-3} mol/l, and the reaction temperature is 296 K.
  * Ethyl diazoacetate (n_{EDA}).

As a result, Eq. (2) takes the form of

$$w_i = \frac{\alpha k_1 [ROC(O)CHN_2][Cu(II)]_\Sigma}{1 + K_2[(R')_2C=CHR'']}.$$

For linear-law chain termination, the concentration of the active form of the catalyst is

$$[Cu(I)] = \frac{\alpha k_1 [ROC(O)CHN_2][Cu(II)]_\Sigma}{k_9(1 + K_2[(R')_2C=CHR''])};$$

that is, at a constant olefin concentration,

$$w_i = k_i[ROC(O)CHN_2][Cu(II)]_\Sigma$$

and $[Cu(I)] = \dfrac{k_i}{k_9}[ROC(O)CHN_2][Cu(II)]_\Sigma$,

where the effective rate constant of active site generation is

$$k_i = \frac{\alpha k_1}{k_9(1 + K_2[(R')_2C=CHR''])}.$$

It follows from Table 5 that the cyclopropanation rate in the case of "long chains" is equal to the nitrogen evolution rate. Another condition for this equality to be true is that the contribution from reaction (VII), which leads to "idle" ROC(O)CHN$_2$ consumption and extra nitrogen evolution, should be small. In the general case,

$$\frac{d[N_2]}{dt} = k_3[ROC(O)CHN_2\cdots Cu(II)]$$

$$+ k_6[ROC(O)CHN_2\cdots Cu(I)] \qquad (3)$$

$$+ k_7[ROC(O)CHN_2][ROC(O)CH:\cdots Cu(I)]$$

$$= w_i + w_{chain} + w_{side}.$$

It can be seen from Fig. 1 that the gas evolution rate at the chain initiation stage (w_i) is well below the gas evolution rate in the developed process (w_{max}). Therefore, the term w_i in expression (3) can be neglected to obtain

$$\frac{d[N_2]}{dt} = k_6[ROC(O)CHN_2\cdots Cu(I)]$$

$$+ k_7[ROC(O)CH:\cdots Cu(I)][ROC(O)CHN_2].$$

Applying quasi-steady-state treatment to [ROC(O)CH:$\cdots$Cu(I)], we obtain

$$[ROC(O)CH:\cdots Cu(I)]$$

$$= \frac{k_6[ROC(O)CHN_2\cdots Cu(I)]}{k_7[ROC(O)CHN_2] + k_8[(R')_2C=CHR'']}.$$

Substitution of the expression for [ROC(O)CH:$\cdots$Cu(I)] into Eq. (3) yields

$$\frac{d[N_2]}{dt} = k_6[ROC(O)CHN_2\cdots Cu(I)]$$

$$+ \frac{k_7[ROC(O)CHN_2]k_6[ROC(O)CHN_2\cdots Cu(I)]}{k_7[ROC(O)CHN_2] + k_8[(R')_2C=CHR'']}$$

$$= (1 + \beta)k_6[ROC(O)CHN_2\cdots Cu(I)].$$

Here, β is the probability of "idle" ROC(O)CHN$_2$ consumption. This function depends on the diazo compound and olefin concentrations:

$$\beta^{-1} = 1 + \frac{k_8[(R')_2C=CHR'']}{k_7[ROC(O)CHN_2]}.$$

Now we will apply quasi-steady-state treatment to the ROC(O)CHN$_2\cdots$Cu(I) concentration. We will take into account that, because of Cu(I) binding into the inert complex (R')$_2$C=CHR''$\cdots$Cu(I), the concentration of free univalent copper is

$$[Cu(I)] = [Cu(I)]_\Sigma/(1 + K_5[(R')_2C=CHR''])\ \text{and}$$

$$\frac{d[ROC(O)CHN_2\cdots Cu(I)]}{dt}$$

$$= k_4[ROC(O)CHN_2][Cu(I)]$$

$$- k_{-4}[ROC(O)CHN_2\cdots Cu(I)]$$

$$- k_6[ROC(O)CHN_2\cdots Cu(I)] = 0,$$

$$[ROC(O)CHN_2\cdots Cu(I)]$$

$$= \frac{k_4[ROC(O)CHN_2][Cu(I)]}{k_{-4} + k_6}.$$

Hence,

$$\frac{d[N_2]}{dt} = (1 + \beta)\frac{k_6}{k_{-4} + k_6}k_4[ROC(O)CHN_2][Cu(I)]$$

$$= (1 + \beta)\gamma k_4[ROC(O)CHN_2][Cu(I)],$$

where $\gamma = \dfrac{k_6}{k_{-4} + k_6}$ is the probability of the formation of a carbene complex from ROC(O)CHN$_2\cdots$Cu(I) or the probability of N$_2$ evolution due to the decomposition of the latter.

The inhibiting effect of complex formation (step (V)) is accounted for by the equality

$$\frac{d[N_2]}{dt} = (1 + \beta)\gamma\frac{k_4[ROC(O)CHN_2][Cu(I)]_\Sigma}{1 + K_5[(R')_2C=CHR'']}.$$

We have already determined the concentration [Cu(I)] using the "long chain" realization condition, so we finally arrive at

$$\frac{d[N_2]}{dt} = w_{N_2} = \alpha(1 + \beta)\gamma$$

$$(4)$$

$$\times \frac{k_1 k_4[ROC(O)CHN_2]^2[Cu(II)]_\Sigma}{k_9(1 + K_2[(R')_2C=CHR''])(1 + K_5[(R')_2C=CHR''])}.$$

It follows from expression (4) that w_{N_2} is directly proportional to the catalyst concentration. According to the data presented in Table 1, the dependence of w_{max} on [Cu(acac)$_2$] is indeed linear, as is predicted by the

kinetic analysis. According to the kinetic scheme, the dependence of w_{N_2} on the ROC(O)CHN$_2$ concentration should be at least quadratic. If the expression for β is taken into account, then, in the limit, w_{N_2} will be proportional to [ROC(O)CHN$_2$]^3 (if k_7[ROC(O)CHN$_2$] $\ll$ k_8[(R')$_2$C=CHR"], then β = const[ROC(O)CHN$_2$]). The rate of reactions involving very reactive olefins would be expected to be a function of [ROC(O)CHN$_2$] to a power of 2 to 3, and this is actually observed experimentally. For styrene, the less reactive olefin, this function is quadratic; for 2,5-dimethylhexa-2,4-diene, the more reactive olefin, w_{max} is proportional to [ROC(O)CHN$_2$]^3.

According to expression (4), the reaction rate decreases as the olefin concentration is increased. Assuming, for the sake of simplicity, that reaction (V) exerts no appreciable effect on the process, we can reduce the equation for the maximum gas evolution rate to

$$w_{N_2} = \frac{\alpha(1 + \beta)\gamma k_1 k_4 [ROC(O)CHN_2]^2 [Cu(II)]_\Sigma}{k_9(1 + K_2[(R')_2C=CHR"])}.$$

The observed dependence of w_{N_2} on the RH concentration is in agreement with the above kinetic scheme. Rearranging the last equation, we obtain

$$\frac{1}{w_{N_2}} = \frac{k_9}{k_{eff}[ROC(O)CHN_2]^2[CuL_2]_\Sigma} \\ + \frac{k_9 K_2[(R')_2C=CHR"]}{k_{eff}[ROC(O)CHN_2]^2[Cu(II)]_\Sigma}, \quad (5)$$

where $k_{eff} = \alpha(1 + \beta)\gamma k_1 k_4$.

Our experiments have demonstrated that w_{max} is independent of the styrene or 2,5-dimethylhexa-2,4-diene concentration if the olefin concentration is higher than 1.5 mol/l. At lower olefin concentrations, such as [(CH$_3$)$_2$C=CHCH=C(CH$_3$)$_2$] = 0–3 mol/l, $1/w_{max}$ is proportional to [(CH$_3$)$_2$C=CHCH=C(CH$_3$)$_2$] (Fig. 2). A similar dependence is observed for styrene ([styrene] = 0–1.5 mol/l).

The above results are in satisfactory agreement with the kinetics of hexene-1 cyclopropanation with ethyl diazoacetate catalyzed by copper(I) trifluoromethanesulfonate [3]. The observed inverse dependence of the reaction rate on the olefin concentration was attributed by the authors of that work [3] to the deactivation of the catalyst caused by its multiplet coordination with the olefin. We demonstrated that this kind of dependence is due to the specific sequence of the elementary steps of the process.

Thus, the kinetic analysis of the above cyclopropanation scheme has provided a plausible explanation for the observed kinetics of the reaction.

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