known alkyl radical disproportionation/recombination ratio in each case.

The differences between the disproportionation/recombination ratios for reactions R2 and R3 are striking. One might expect that disproportionation would be more important for (R2) than (R3) on thermodynamic grounds, as (R2a) is a few kcal  $mol^{-1}$ more exothermic than (R2c) in each case, whereas the corresponding alkyl radical disproportionations (R3b) are approximately 20 kcal mol<sup>-1</sup> less exothermic than the recombinations (R3a). $^{60}$ 

(60) Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. Chem. Rev. 1969, 69, 279.

The alternative disproportionations, R2b, are approximately 30 kcal  $mol^{-1}$  less exothermic than the (R2a). However, it is not clear that the relative exothermicities of the possible reactive channels R2a-c should affect their relative importance. (R2) is expected to proceed without a barrier to reaction and the relative importance of (R2a-c) will be very sensitive to details of the potential energy surface for the system. To our knowledge, no detailed calculations of the potential energy surface for (R2) have been performed.

Registry No. CH<sub>3</sub>CHO, 75-07-0; C<sub>2</sub>H<sub>3</sub>CHO, 123-38-6; n-C<sub>3</sub>H<sub>7</sub>CHO, 123-72-8; *i*-C<sub>3</sub>H<sub>7</sub>CHO, 78-84-2; *t*-C<sub>4</sub>H<sub>9</sub>CHO, 630-19-3; HCO, 2597-44-6; CH<sub>3</sub>, 2229-07-4; C<sub>2</sub>H<sub>5</sub>, 2025-56-1; n-C<sub>3</sub>H<sub>7</sub>, 2143-61-5; i-C<sub>3</sub>H<sub>7</sub>, 2025-55-0; t-C<sub>4</sub>H<sub>9</sub>, 1605-73-8.

# Oxidation of Glyoxylic Acid to Formic Acid in the Belousov–Zhabotinsky Reaction. A <sup>1</sup>H NMR Study<sup>1</sup>

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We describe experimental evidence obtained by <sup>1</sup>H NMR spectroscopy which shows that, when a malonic acid BZ reaction is perturbed by glyoxylic acid in the concentration range  $10^{-1}-10^{-3}$  M, the production of formic acid is observed. Since the oscillator without added glyoxylic acid does not show any production of formic acid, and since formic acid itself was found to be inert when added to a BZ system, we believe that glyoxylic acid cannot be a major intermediate in the malonic acid BZ reaction. Also when hydroxyacetic acid is added in the concentration range  $10^{-1}-10^{-2}$  M to a malonic acid BZ reaction formic acid was found as an end product. These results indicate that glyoxylic acid is not an intermediate in the malonic acid BZ reaction and we suggest a reaction path for malonic acid oxidation under BZ conditions starting from malonic acid via tartronic acid to mesoxalic acid and finally to carbon dioxide. We also show that the recently proposed hydrogen sulfite test to determine quantitatively glyoxylic acid in the BZ reaction is not specific for this compound: also mesoxalic acid reacts almost quantitatively with the hydrogen sulfite ion.

#### Introduction

The cerium-catalyzed malonic acid Belousov<sup>2</sup>-Zhabotinsky<sup>3</sup> (BZ) reaction is undoubtedly among the most investigated and best understood<sup>4</sup> chemical oscillating systems. While this is particularly true for the inorganic reaction subset<sup>5,6</sup> of the BZ reaction, the knowledge about the reaction path and the kinetics of the malonic acid oxidation to carbon dioxide under BZ conditions is still relatively poor.

From stoichiometric observations<sup>7,8</sup> it has been known for many years that when cerium(IV) oxidizes malonic acid (MA) in isolation only two of the carbons appear as carbon dioxide and that one (probably the center carbon) is oxidized only to formic acid (FA) by the reaction sequence S1 with tartronic acid (TTA) and glyoxylic acid (GOA) as assumed intermediates.9

$$MA \rightarrow TTA \rightarrow GOA \rightarrow FA$$
 (S1)

Field, Körös, and Noyes (FKN)<sup>10</sup> postulated that stoichiometry in their first effort to explain the oscillations. They proposed the formation of bromomalonic acid (BrMA) and formic acid in a stoichiometric ratio of 3:2. However, several investigations showed by using quite different techniques<sup>11-13</sup> that formic acid is not an

<sup>(1)</sup> This is paper No. 76 in the series "Chemical Oscillations and Instabilities"; No. 75 is Bar-Eli, K.; Noyes, R. M. J. Chem. Phys. 1987, 86, 1927.

<sup>(2)</sup> Belousov, B. P. Ref. Radiats. Med., Moscow, 1959, 145. A translation of an earlier version of Belousov's paper into English can be found in: Os-cillations and Traveling Waves in Chemical Systems, Field, R. J., Burger, M., Eds.; Wiley: New York, 1985.

<sup>(3)</sup> Zhabotinsky, A. M. Dokl. Akad. Nauk SSSR 1964, 157, 392. For a review of Zhabotinsky's earlier work see: Zhabotinsky, A. M. In Oscillations and Traveling Waves in Chemical Systems, Field, R. J., Burger, M., Eds.; Wiley: New York, 1985.

<sup>(4)</sup> See contributions by Field, R. J.; Tyson, J. J.; Epstein, I. R.; Orban, (4) See Control Information of a Hold, R. S., 1980, S. S., Epstein, F. R., Orbein, M., Winfree, A. T. In Oscillations and Traveling Waves in Chemical Systems, Field, R. J., Burger, M., Eds.; Wiley: New York, 1985.
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<sup>(11)</sup> Bornmann, L.; Busse, H.; Hess, B. Z. Naturforsch. 1973, 28c, 514.

 <sup>(12)</sup> Brusa, M. A.; Colussi, A. J. Int. J. Chem. Kinet. 1983, 15, 1335.
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end product in the malonic acid BZ reaction and is kinetically inert once formed under BZ conditions. Using NMR spectroscopy, our detection limit for formic acid was better than  $10^{-4}$  M.<sup>13</sup> The work of Bornmann et al.<sup>11</sup> showed in addition by isotopic labeling of the malonic acid that the center carbon atom began to appear as carbon dioxide already in the early stages of the BZ reaction. Jwo and Noyes<sup>9</sup> tried to avoid the discrepancy by invoking a 2-equiv oxidation of formic acid by bromine or HOBr.

$$Br_2 + HCOOH \rightarrow 2Br^- + CO_2 + 2H^+$$
(1)

On the other hand, a NMR study of the methylmalonic acid (MeMA) BZ reaction<sup>14</sup> showed that bromomethylmalonic acid (BrMeMA) and acetic acid are formed as end products in a stoichiometric ratio of 3:2, precisely as originally proposed by FKN for the analogous products BrMA and formic acid!

Several authors have stressed the importance of glyoxylic acid as a major intermediate in the malonic acid BZ reaction.9,15-17 On the basis of Jwo and Noyes' results<sup>9</sup> that there seems to be no evidence that mesoxalic acid is produced from malonic acid, Burger and Rácz<sup>18</sup> used the sulfite-carbonyl reaction<sup>19</sup> to determine quantitatively glyoxylic acid.

In this paper we describe experimental evidence obtained by <sup>1</sup>H NMR spectroscopy that when a malonic acid BZ reaction is perturbed by glyoxylic acid in the concentration range 10<sup>-1</sup>-10<sup>-3</sup> M and by hydroxyacetic acid in the concentration range  $10^{-1}$ - $10^{-2}$ M, the production of formic acid is observed. If glyoxylic acid would be a major intermediate, formic acid should accumulate<sup>11-13</sup> as a result of the glyoxylic acid oxidation and formic acid should be observed as a major end product in the unperturbed malonic acid BZ reaction. Since formic acid is not observed as an end product in the malonic acid BZ reaction and since we do observe formic acid in the glyoxylic acid perturbed BZ system, we have doubts that glyoxylic acid is a major intermediate in the malonic acid BZ reaction. We will also show that mesoxalic acid reacts almost quantitatively with the hydrogen sulfite ion, indicating that the procedure of Burger and Racz<sup>18</sup> can be equally applied to the determination of mesoxalic acid and is therefore not specific to glyoxylic acid.

#### Materials and Method

Proton high-resolution NMR spectra were obtained on a pulse FT NMR spectrometer, Bruker CXP200, with a <sup>1</sup>H frequency of 200 MHz. To keep the solvent proton peak as low as possible the processes studied were either performed in 1 M  $D_2SO_4$  (in  $D_2O$ ) or, when 1 M  $H_2SO_4$  (in  $H_2O$ ) was used as a solvent, the solvent proton peak was lowered by a suppression technique.<sup>20</sup>

The BZ reaction was either run in a thermostatted (25 °C) glass reactor (150-mL reaction volume) with magnetic stirring (approximate stirring rate 500 rpm) or directly in the probe of the NMR instrument. In the latter case spectra were obtained both with sample spinning and stirring throughout the experiment. When the reaction was run in the 150-mL glass reactor, 10-mL samples were taken before the start of the oscillations with only the organic acids(s) dissolved, i.e. before addition of bromate (KBrO<sub>3</sub>, Merck, Darmstadt) and cerium(IV) ion ((NH<sub>4</sub>)<sub>2</sub>Ce-(NO<sub>3</sub>)<sub>6</sub>, Merck, Darmstadt), and after the oscillations had stopped. Then the samples were deep frozen, stored, and finally analyzed by NMR with the sample spinning in the magnetic field.

All chemicals used were of analytical grade, except the glyoxylic acid (Sigma) which was about 98%. Both glyoxylic acid and mesoxalic acid (Sigma) were stored in a deep-freezer well below 0 °C. All chemicals were used without further purification.





Figure 1. (A) Proton NMR spectrum of 0.28 M malonic acid, 0.14 M glyoxylic acid, and  $2.1 \times 10^{-3}$  M Ce(IV) in 1 M D<sub>2</sub>SO<sub>4</sub>. (1) is the water peak, (2) refers to glyoxylic acid, and (3) is the contribution from the hydrogen atoms attached to the central carbon atom in the malonic acid. Relative peak areas in arbitrary units: (2) 27; (3) 100. (B) Proton NMR spectrum of sample described in (A) 43 min after addition of KBrO<sub>3</sub>. (4) is the formic acid peak. Relative peak areas: (2) 4.4; (3) 6.5; (4) 2.0. We noted that the relative position of water peak 1 is dependent upon pH. At higher pH values the position of (1) can be found to the right of the glyoxylic acid peak.

The reaction between mesoxalic acid and the hydrogen sulfite ion was studied by using the iodometric method of Burger and Rácz.<sup>18</sup> To  $1.5 \times 10^{-3}$  mol of sodium sulfite, different amounts of mesoxalic acid in the range  $(1.5-11.2) \times 10^{-4}$  mol were added. The pH was adjusted to 2-3 with 20% acetic acid, and the excess sulfite ion concentration was determined by titration with a 0.05 M iodine solution using starch for detection of the end point. When the end point was reached, solid sodium bicarbonate was added to raise the pH to about 7 and to hydrolize the addition product between hydrogen sulfite ion and the central carbonyl group of mesoxalic acid. Then the freed hydrogen sulfite ions were determined by titration with the iodine solution and compared with the amount of mesoxalic acid added initially.

#### Results

Influence of Glyoxylic Acid on the Malonic Acid BZ Reaction. We made assignments of reactant and product peaks when the reaction is performed in  $D_2SO_4$  (in  $D_2O$ ) together with glyoxylic acid. Figure 1A shows the proton NMR spectrum of 0.28 M malonic acid, 0.14 M glyoxylic acid, and  $2.1 \times 10^{-3}$  M Ce(IV) in 1 M  $D_2SO_4$ . Figure 1B shows the spectrum 40 min after bromate has been added. We observed a new peak (4) which was

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Figure 2. (A) Proton NMR spectrum of 0.28 M malonic acid and  $5 \times 10^{-3}$  M glyoxylic acid in 1 M sulfuric acid obtained by using the "water-proton suppression technique" (ref 20). (1) is the residual water proton peak; (2) is the contribution from the malonic acid. Relative peak areas in arbitrary units: (1) 100; (2) 5.550. (B) Proton NMR spectrum of (A) 50 min after addition of cerium(IV) and KBrO<sub>3</sub> when the oscillations have just stopped. (3) is the formic acid peak. Peaks 4–8 have not been identified yet. The relative peak areas in arbitrary units: (1) 100; (2) 2.119; (3) 0.011.

identified as formic acid by adding formic acid to the sample.

We also performed the reaction in a 150-mL glass reactor in 1 M sulfuric acid. To increase the sensitivity of the NMR method, we lowered the water solvent proton peak by a suppression technique.<sup>20</sup> Figure 2 shows a <sup>1</sup>H NMR spectrum of a mixture of malonic and glyoxylic acid in 1 M H<sub>2</sub>SO<sub>4</sub> obtained by using the "water-suppression technique"<sup>20</sup> before starting the oscillations (Figure 2A) and after the oscillations have stopped (Figure 2B). Also here we observe the production of formic acid in the presence of glyoxylic acid (Figure 2B, peak 3).

Figure 3 shows the effect on the oscillations when various initial amounts of glyoxylic acid are added to the cerium-catalyzed malonic acid BZ reaction. We observe a slight decrease in the induction period length and an increase in frequency when the amount of glyoxylic acid is increased. This is in agreement with reports of Kaner and Epstein<sup>15</sup> and of Körös and Varga.<sup>21</sup> At high initial glyoxylic acid concentrations the oscillations become damped.

Figure 4 shows the estimated amounts of formic acid produced by the BZ oscillators of Figure 3. We found that as a *mean* about 20% of the initially present glyoxylic acid was oxidized to formic acid.

Influence of Hydroxyacetic Acid on the Malonic Acid BZ Reaction. Three different hydroxyacetic acid concentrations were added to the BZ reaction (0.1, 0.05, and 0.01 M). We found that



**Figure 3.** Influence of added glyoxylic acid to a malonic acid BZ reaction in 1 M sulfuric acid at 25 °C. Initial concentrations:  $[(NH_4)_2Ce(NO_3)_6]$ = 2.1 × 10<sup>-3</sup> M, [malonic acid] = 0.28 M, and [KBrO<sub>3</sub>] = 0.1 M. Initial glyoxylic acid concentrations: (A) no glyoxylic acid added; (B) 1 × 10<sup>-3</sup> M; (C) 5 × 10<sup>-3</sup> M; (D) 1.0 × 10<sup>-2</sup> M; (E) 5.0 × 10<sup>-2</sup> M; (F) 0.1 M.

the behavior of hydroxyacetic acid is very similar to glyoxylic acid, i.e. the frequency of the malonic acid oscillator is increased at higher initial hydroxyacetic acid concentrations and the oscillations become damped instead of stopping with full amplitude (Figure 5).

Analysis by <sup>1</sup>H NMR shows that hydroxyacetic acid is very slowly consumed and that only 50–70% of the hydroxyacetic acid initially added to the 150-mL reactor was consumed during a 3–4-h period. Figure 6 shows a typical <sup>1</sup>H NMR spectrum for added hydroxyacetic acid, while Figure 7 shows the estimated formic acid production as a function of initial hydroxyacetic acid concentration.

The Sulfite-Mesoxalic Acid Addition Reaction. Burger and Rácz<sup>18</sup> used the carbonyl sulfite addition reaction to determine quantitatively the glyoxylic acid in the BZ reaction. We performed the same procedure with mesoxalic acid (for procedure see the Materials and Method section) and found (Figure 8) that mesoxalic acid adds hydrogen sulfite almost quantitatively. The implications of this observation will be discussed in the next section.

#### Discussion

The fact that formic acid is not observed as an end product in the BZ reaction, while added glyoxylic acid in concentrations as low as  $10^{-3}$  M produces formic acid makes it doubtful that glyoxylic acid is a main flow-through intermediate in the BZ reaction. The extrapolated solid line through the origin in Figure 4 suggests that about 25% (the mean of the three lowest glyoxylic acid concentrations) of the initial available glyoxylic acid is oxidized to formic acid; the rest is probably oxidized to carbon dioxide. These data are consistent with two parallel processes P1 and P2 where glyoxylic acid (GOA) is oxidized to formic acid,

$$GOA \xrightarrow{Ce^{4+}} FA \tag{P1}$$

$$GOA \xrightarrow{B_{7}O_{3}^{-}} CO_{2}$$
 (P2)

FA (probably Ce(IV) is involved), and carbon dioxide (bromate ion and other bromo-oxygen species are involved), respectively.

<sup>(21)</sup> Körös, E.; Varga, M. J. Phys. Chem. 1982, 86, 4839.



Figure 4. Formic acid production for the glyoxylic acid (GOA) perturbed BZ systems of Figure 3. Solid points with increasing GOA concentrations correspond to systems B-F of Figure 3, respectively. Final formic acid concentrations were estimated by assigning one single proton to formic acid peak 3 (see Figure 2B) and two protons to malonic acid peak 2 (see Figure 2A). Since the initial malonic acid concentration is known (0.28 M), the final formic acid concentrations can be calculated by assuming that the solvent proton peak is approximately constant. The solid line is eye-balled to go through origin and the three points with lowest initial glyoxylic acid concentration. This line corresponds to when about 25% of all added glyoxylic acid is converted to formic acid.



Figure 5. Influence of added hydroxyacetic acid to malonic acid BZ systems in 1 M sulfuric acid at 25 °C. Same initial concentrations of Ce(IV), malonic acid, and bromate as in Figure 3. Initial hydroxyacetic acid concentrations: (A) no hydroxyacetic acid added; (B)  $1.0 \times 10^{-2}$  M; (C)  $5.0 \times 10^{-2}$  M; (D) 0.1 M.

When prosesses P1 and P2 are approximated as pseudo-first-order reactions, the relative amounts of formic acid and carbon dioxide are constant and the formic acid generated is proportional to the initial glyoxylic acid concentration as indicated by the solid line in Figure 4. These results stand in some contrast to a previous report of Noszticzius and Bodiss<sup>16</sup> who found that, even in the presence of Ce(IV), the oxidation of glyoxylic acid goes completely



Figure 6. (A) Proton NMR spectrum of hydroxyacetic acid and malonic acid-sulfuric acid at 25 °C obtained by using the water-proton suppression technique (ref 20). Initial concentrations: [malonic acid] = 0.28 M, [hydroxyacetic acid] = 0.05 M. (1) is the residual water proton peak, (2) is the contribution of the malonic acid, and (3) is the contribution from the hydrogen atoms attached to carbon in hydroxyacetic acid. Relative peak areas in arbitrary units: (1) 100; (2) 5.861; (3) 0.426. (B) Proton NMR spectrum of (A) 80 min after cerium(IV) and bromate addition just when oscillations have stopped. (4) is the formic acid base. Peaks 5-8 are not identified but are very similar to the corresponding product peaks of added glyoxylic acid (Figure 2B). Relative peak areas in aribitary units: (1) 100; (2) 2.648; (3) 0.129; (4) 0.027.

to carbon dioxide. They used a gas analytical technique that determines the amount of carbon dioxide produced from a given amount of glyoxylic acid. However, the main difference between our system and that of Noszticzius and Bodiss<sup>16</sup> is that we are primarily studying a glyoxylic acid perturbed *malonic acid* oscillator, while Noszticzius and Bodiss<sup>16</sup> were studying a glyoxylic *acid* oscillator. The glyoxylic acid oscillator has considerably less oscillations, i.e. less Ce(IV) spikes than the malonic acid oscillator and therefore the probability of reacting according to process P1 is less for the pure glyoxylic acid oscillator than for the glyoxylic acid-perturbed malonic acid system.

We therefore believe that according to our experiments (Figure 4) about 25% of the glyoxylic acid present as a main flow intermediate should be oxidized to formic acid. Since this is not the case (i.e. no formic acid is observed in the malonic acid BZ reaction) we have serious doubts that glyoxylic acid is a major intermediate in the malonic acid BZ reaction.

Also hydroxyacetic acid is apparently not an intermediate in the malonic acid oxidation because of the production of formic acid. Comparing the final <sup>1</sup>H NMR spectra (Figure 6B and Figure 2B) indicates that the hydroxyacetic acid oxidation proceeds via glyoxylic acid. This is further supported by the similar behavior



Figure 7. Formic acid production of the hydroxyacetic acid perturbed BZ oscillators of Figure 5 (B-C). Same estimation procedure as for Figure 4.



Figure 8. The straight line A shows the theoretical excess sulfite ion (in moles) when mesoxalic acid is added. Solid points represent experimental results. The dashed line B shows the theoretical amount of sulfite ion after hydrolysis of the addition product between sulfite ion and mesoxalic acid. The open squares are the experimental results.

hydroxyacetic acid and glyoxylic acid have on the malonic acid oscillator (Figure 3 and Figure 5).

However, if hydroxyacetic acid and glyoxylic acid are not intermediates in the malonic acid BZ reaction, what alternative route does the malonic acid oxidation then take? The first two-equivalent oxidation goes almost certainly to tartronic acid, although there exists presently no direct experimental evidence of that species in the malonic acid BZ reaction. The only other possibility would be hydroxyacetic acid, but we exclude this species because of the production of formic acid. In the presence of only cerium(IV), oxidation of tartronic acid goes via glyoxylic acid to formic acid as proposed by sequence S1. We now believe that in the presence of the oxybromine species the path of tartronic acid oxidation is diverted to mesoxalic acid. The work of Jwo and Noyes<sup>9</sup> then implies that mesoxalic acid is rapidly oxidized (probably mostly) to carbon dioxide. Although the mesoxalic acid oxidation is relatively rapid, we anticipate that this reaction takes place in steps.

Figure 9 summarizes our expected behavior of malonic acid oxidation in the presence of cerium(IV) and in the presence of bromate and cerium(IV). This interpretation is consistent with the observation of Bornmann et al.<sup>11</sup> that all three carbon atoms from malonic acid appear as carbon dioxide; it is also in agreement with recent experimental results of Försterling et al.<sup>22</sup> which



Figure 9. Schematic representation of proposed reaction path of malonic acid oxidation. In the presence of only cerium(IV), formic acid (besides of carbon dioxide) is produced. When bromate ion is also present (BZ conditions), tartronic acid is oxidized to mesoxalic acid, which then is completely oxidized to carbon dioxide. This explains why formic acid is not observed in malonic acid BZ systems, but only when glyoxylic acid is added to the BZ reaction.

indicate a larger rate of carbon dioxide production when compared with the original  $FKN^{10}$  approach.

Our interpretation is also consistent with the results obtained by Burger and Racz.<sup>18</sup> These authors added hydrogen sulfite ion to a malonic acid BZ reaction and measured the amount of added carbonyl compounds to the hydrogen sulfite ion, claiming that the addition reaction was only due to glyoxylic acid. The results from our Figure 8 indicate that mesoxalic acid can be considered as an alternative intermediate in the malonic acid BZ reaction.

Recently, Ouyang et al.<sup>23</sup> describe experiments and cite unpublished work which seem to indicate that not all of the malonic acid ends up as carbon dioxide, but that a significant amount ends up as carbon monoxide. The work of Barkin et al.<sup>24</sup> indicates that possible CO formation is not due to the cerium(IV) oxidation of malonic acid, but it appears that also in this case oxidation by the oxybromine species might be responsible for possible CO production. An important task in this respect is to identify the source of CO formed. Mesoxalic acid might be such a source, as the determined stoichiometry by Jwo<sup>25</sup> of the cerium(IV)mesoxalic acid reaction indicates.

Unfortunately, mesoxalic acid cannot be detected directly by <sup>1</sup>H NMR spectroscopy; but we hope to return to the question of possible mesoxalic acid identification and reactions (and perhaps also of other organic intermediates) in a further study.<sup>26</sup>

Finally, we note that when one of the central hydrogen atoms in the malonic acid is substituted by a methyl group, the "diversion" to the corresponding keto acid is prohibited, and in this case the products of the cerium-catalyzed BZ reaction are bromomethylmalonic acid and acetic acid, precisely as predicted by the FKN theory!<sup>13</sup>

Even when only glyoxylic acid is used as an organic substrate, the work of Kaner and Epstein<sup>15</sup> and of Noszticzius and Bodiss<sup>16</sup> have shown that a BZ oscillator can be obtained. In such a system

<sup>(22)</sup> Försterling, H. D.; Idstein, H.; Pachl, R.; Schreiber, H. Z. Naturforsch. 1984, 39a, 993

<sup>(23)</sup> Ouyang, Q.; Tam, W. Y.; DeKepper, P.; McCormick, W. D.; Nosz-ticzius, Z.; Swinney, H. L. J. Phys. Chem. 1987, 91, 2181. (24) Barkin, S.; Bixon, M.; Noyes, R. M.; Bar-Eli, K. Int. J. Chem. Kinet.

<sup>1978, 10, 619</sup> 

<sup>(25)</sup> Ph.D. Thesis of J. J. Jwo, available from Xerox University Microfilms by writing to Dissertation Copies, P.O. Box 1764, Ann Arbor, MI 48106 and asking for No. 75-3888. The stoichiometry of the Ce(IV)–MOA reaction is given in Table I, p 36. Complete oxidation of MOA by Ce(IV) requires 4 mol of Ce(IV) per mol of MOA. Jwo reports 3.4 mol of Ce(IV) per mol of MOA

<sup>(26)</sup> Brusa, M. A.; Perissinotti, L. J.; Colussi, A. J. J. Phys. Chem. 1985, 89, 1572. These authors have identified malonyl radicals in BZ systems by ESR under stopped-flow conditions.

two well-defined oscillatory regimes separated by a quiescent region have recently been found for batch conditions,<sup>27</sup> where the size of the quiescent region is approximately on the order of each of the two oscillating regions. Although the glyoxylic BZ oscillator

(27) Ruoff, P.; Körös, E.; Hansen, E. W. React. Kinet. Catal. Lett., submitted for publication.

is an interesting example, this system appears now to be unrelated to the malonic acid BZ reaction.

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## **Reactions of Energetic Carbon-11 with Benzene Leading to Acetylene**

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The reactions of energetic carbon-11 leading to acetylene were studied in specifically deuteriated benzene and 50/50 mixtures of perdeuteriated and perprotonated benzenes and alkanes. The contributions of intermolecular and intramolecular mechanisms in acetylene formation in benzene were deduced from the relative yields of the three isotopic acetylenes  ${}^{(11)}C_2H_2$ ,  ${}^{(11)}C_2H_2$ ,  ${}^{(11)}C_2H_2$ , and  ${}^{(11)}C_2D_2$ . High-energy stripping and abstraction reactions of  ${}^{(11)}C_2$  and  ${}^{(11)}C_2H$  ions appear to account for acetylene formed via an intermolecular pathway. After correction for the intermolecular mechanism, the remaining acetylene is formed mainly by direct insertion ( $\sigma$  or  $\pi$ ) plus a small contribution from a mechanism involving random selection of H or D in the benzene molecule.

### Introduction

Recent investigations of the reactions of energetic carbon-11 generated by nuclear transformations have focused on isotope effects, the electronic state,<sup>1</sup> the influence of electron density and bond polarization on product yielding steps,<sup>2</sup> and on the energetics and reaction mechanisms leading to labeled products.<sup>3</sup> The insertion of hot and thermalized atomic <sup>11</sup>C and secondary intermediates (e.g., <sup>11</sup>CH) into C-H bonds, followed by the decomposition of an energy-rich intermediate, has been mechanistically convenient for explaining the formation of (<sup>11</sup>C)acetylene and other (<sup>11</sup>C)products.<sup>1-4</sup> The involvement of high-energy stripping and abstraction reactions<sup>5</sup> leading to (<sup>11</sup>C)acetylene was suggested<sup>6</sup> by the appearance of <sup>(11)</sup>C<sub>2</sub>HD in reaction mixtures containing equimolar mixtures of perdeuteriated and perprotonated alkanes and benzene. Although  ${}^{(11)}C_2H_2$  and  ${}^{(11)}C_2D_2$  were the predominant products,  ${}^{4c,f,7}$  the formation of  ${}^{(11)}C_2HD$  cannot be accounted for if the mechanism of acetylene formation is solely intramolecular and derived entirely from energetic <sup>11</sup>C insertion reactions. In substrates of specifically deuteriated alkanes the yield of mixed acetylene increased.<sup>7</sup> In the latter systems, the formation of  $^{(11)}C_2HD$  can be accounted for if H or D migration occurs during the lifetime of the intermediate. Presumably the preponderant decomposition mode does not involve intramolecular rearrangement as a prior step.

Lemmon and co-workers<sup>8</sup> reported observations of acetylene formation in hot carbon systems that did not rule out a high-energy stripping mechanism. Rose and Mackay9 reported evidence indicating that hot atomic <sup>11</sup>C can remove groups such as <sup>11</sup>CH<sub>2</sub> as a single unit in a rapid reaction leading to acetylene which does not involve formation of an equilibrated intermediate. Pohlit<sup>8a</sup> and Williams<sup>10</sup> suggested the involvement of C<sub>2</sub>H in the formation of phenylacetylene in the reactions of accelerated <sup>14</sup>C and recoil <sup>11</sup>C in solid and liquid benzene, respectively.

This communication addresses the role of high-energy stripping and abstraction reactions, and the question of intramolecular and intermolecular formation of (<sup>11</sup>C)acetylene in specifically deuteriated benzenes.

#### **Experimental Section**

The reacting systems were contained in quartz vessels and subjected to a diffused beam of 33-MeV protons at the BNL 60-in. cyclotron to produce the  ${}^{12}C(p,pn){}^{11}C$  and the  ${}^{16}O(p,pn\alpha){}^{11}C$ nuclear reactions.<sup>1d</sup> Experimental conditions are footnoted in Tables I and II. The irradiation dose was  $1.74 \times 10^{-4}$  eV·molecule<sup>-1</sup>· $\mu$ A<sup>-1</sup>·s<sup>-1</sup> as determined by acetylene to benzene dosimetry.<sup>11</sup> Typically beam intensities were 1  $\mu$ A with a 200-s exposure time. The  $(^{11}C)$  acetylenes were isolated from the bulk reaction mixture by gas chromatography with a Porapak R column<sup>1d</sup> after the addition of a 1%  $C_2(DH)$  carrier mixture consisting of  $C_2H_2$ ,  $C_2HD$ , and  $C_2D_2$  in a relative concentration of 43.3%, 20.3%, and 36.3%, respectively. The isolated acetylenes were reduced to the corresponding ethylenes with acidic chromic chloride, with an efficiency of 83-90%. The ethylenes were radioassayed, using two 25-ft columns of 30-60 mesh firebrick coated with 25%

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