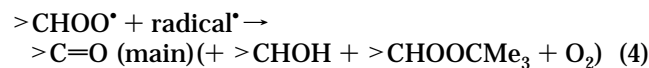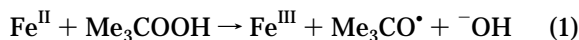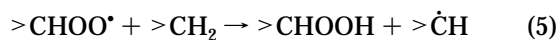# A Radical Account of "Oxygenated Fenton Chemistry" [1]

In a recent Account, Sawyer et al.[3] have summarized much of their earlier work on what they refer to as "oxygenated Fenton chemistry". The overall reaction is perfectly straighforward and noncontroversial. In the presence of dioxygen, a mixture containing an iron catalyst (generally Fe^{II}), Me_3COOH (or H_2O_2), and a hydrocarbon in acetonitrile at room temperature yields mainly the ketone derived from the hydrocarbon together with smaller quantities of other oxidation products such as the corresponding alcohol. The proposed mechanism for these oxidations is anything but straightforward and deserves to be challenged. The most remarkable claim[3] is that "Fenton reagents *do not produce* [Sawyer's italics]... free carbon radicals...".[4] This ignores a wealth of earlier work on iron/hydroperoxide/hydrocarbon chemistry.[7] Moreover, it also ignores classical free radical and autoxidation chemistry[8] which we demonstrate herein, by means of a few carefully selected experiments, provide both a simpler reaction mechanism and one in concordance with *known* free radical kinetics. This (classical) mechanism is shown in abbreviated form in reactions 1–5 and will be further elaborated when necessary.
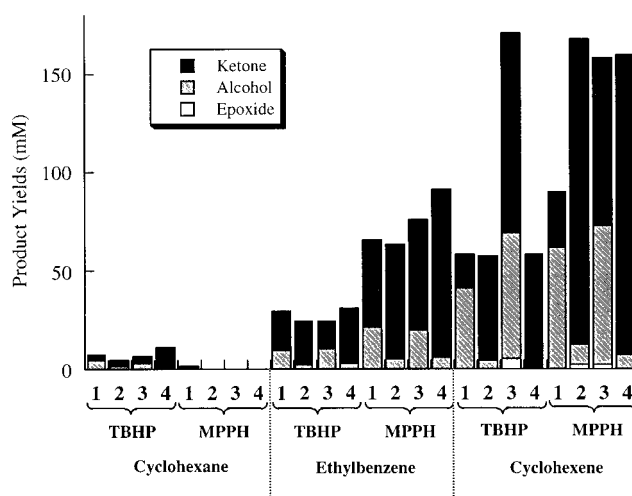
Cyclohexane

$$Fe^{II} + Me_3COOH \rightarrow Fe^{III} + Me_3CO^{\bullet} + {}^-OH \quad (1)$$

$$Me_3CO^{\bullet} + >CH_2 \rightarrow Me_3COH + >\dot{C}H \quad (2)$$

$$>\dot{C}H + O_2 \rightarrow >CHOO^{\bullet} \quad (3)$$

$$>CHOO^{\bullet} + radical^{\bullet} \rightarrow$$
$$>C=O \ (main)(+ >CHOH + >CHOOCMe_3 + O_2) \quad (4)$$

Ethylbenzene and Cyclohexene

$$>CHOO^{\bullet} + >CH_2 \rightarrow >CHOOH + >\dot{C}H \quad (5)$$

To distinguish between Sawyer's nonradical mechanism and reactions 1–5, we have utilized four of his catalysts, viz. ferric chloride ($Fe^{III}Cl_3$, **1**), iron(II) tetrakis(triphenylphosphine oxide) ($Fe^{II}(OPPh_3)_4$, **2**), iron(II) bis(2,2′-bipyridyl) ($Fe^{II}(bpy)_2$, **3**), and iron(II) bis(picolinate) ($Fe^{II}(PA)_2$, **4**), and three of his substrates, viz. cyclohexane, ethylbenzene, and cyclohexene. Reactions were run *in duplicate* with constant stirring at room temperature under 1 atm of oxygen for 18 h (the conditions given in the original report[9] since there is little reaction with cyclohexane after the 3 h indicated in Table 2 of the Account[3]). The reagent concentrations were also the same as those employed in some of the previous work,[3,9] viz. 1.0 M hydrocarbon, 10 mM catalyst, and 20 mM Me_3COOH (TBHP) *or* 20 mM $PhCH_2CMe_2OOH$ (MPPH, see below). The solvents were acetonitrile (**1** and **3**), pyridine/acetonitrile (1:4 mole ratio) (**2**), and pyridine/acetic acid (2:1 mole ratio) (**4**) as described originally.[9] Reactions were quenched with an
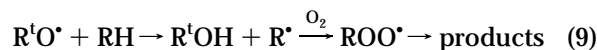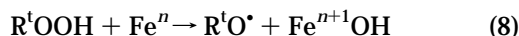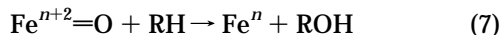

FIGURE 1. Oxidation of cyclohexane, ethylbenzene, and cyclohexene by iron catalysts **1**–**4** and two *tert*-alkyl hydroperoxides, TBHP and MPPH, at room temperature under an atmosphere of oxygen for 18 h.

excess of triphenylphosphine (to convert hydroperoxides to the corresponding alcohols) and analyzed on a Hewlett-Packard 5890 Series II gas chromatograph (HP Ultra 1 cross-linked methyl silicone column, 12m × 0.2 mm × 0.33 μm; temperature program: 40 °C for 7 min, 15 °C/min to 250 °C, 250 °C for 5 min) using 1,4-dibromobenzene as an internal standard. Data analyses were performed using an HP Chemstation.. The absolute product yields[10] are shown in bar graph form in Figure 1.

By examining first the 12 bar graphs from the TBHP experiments, it is clear that the total product yield increases along the series: cyclohexane < ethylbenzene < cyclohexene and that, with a few exceptions, the total yields for each substrate are *roughly* independent of the catalyst. With cyclohexane the product yields are less than or equal to that of the initial catalyst, viz., 10 mM (overall average from our eight experiments = 7.5 vs 10 mM from Sawyer's *et al.'s* original four experiments[9]), with ethylbenzene the average product yield rises to 25.6 mM (vs 39.8 mM[9]) and with cyclohexene to 86.0 mM (vs 107.9 mM[9]). *It is totally unnecessary to invoke catalyst "turnover" to explain these results since they can be simply accounted for on the basis of the relative importance of reaction 5.* For cyclohexane,[11] ethylbenzene,[12] and cyclohexene[12] the values for k_5 are 0.048, 1.1, and 6.1 $M^{-1} s^{-1}$, respectively. Thus, reaction 5 is insignificant for cyclohexane, is relevant for ethylbenzene, and becomes important for cyclohexene. We can make a *rough* correction for hydrocarbon oxidation via *tert*-butoxyl radicals (reaction 2) by subtracting the average product yield for cyclohexane (7.5 mM) from the average product yields for cyclohexene (86.1 mM) and ethylbenzene (25.6 mM). With this correction, the ratio of cyclohexene/ethylbenzene products which probably arise mainly from autoxidation, i.e. hydrogen atom abstraction by peroxyl radicals (reaction 5), is $(86.1-7.5)/(25.6-7.5) = 4.3$ (vs 3.3 from the original work[9]). The ratio of 4.3 is in rather satisfactory agreement with the ratio expected on the basis of the relative magnitudes of the k_5 values for cyclohexene and ethylbenzene, viz.[12] $6.1/1.1 = 5.5$.

We introduced MPPH as a mechanistic probe[13] in *tert*-alkyl hydroperoxide/iron catalyst/alkane systems to distin-

guish between alkane oxidations via high-valent iron–oxo species (as favored by many others) and oxidations which occurred via hydrogen atom abstraction from the alkane by freely diffusing alkoxyl radicals; i.e., to distinguish between the reaction pathway 6, 7 and pathway 8, 9 (where Fe^n is Fe^{II} or Fe^{III}).

$$R^tOOH + Fe^n \rightarrow R^tOH + Fe^{n+2}{=}O \qquad (6)$$

$$Fe^{n+2}{=}O + RH \rightarrow Fe^n + ROH \qquad (7)$$

$$R^tOOH + Fe^n \rightarrow R^tO^\bullet + Fe^{n+1}OH \qquad (8)$$

$$R^tO^\bullet + RH \rightarrow R^tOH + R^\bullet \xrightarrow{O_2} ROO^\bullet \rightarrow products \quad (9)$$

The probe hydroperoxide, MPPH, relies on the fact that β-scission of the corresponding *tert*-alkoxyl radical, reaction 10,

$$PhCH_2CMe_2O^\bullet \rightarrow PhCH_2^\bullet + Me_2CO \qquad (10)$$

is much too rapid ($k_{10} \sim 2 \times 10^8$ s^{-1}) for there to be any hydrogen atom abstraction from cyclohexane (even at 1 M) analogous to reactions 2 and 9 ($k_2 = k_9 = 1.2 \times 10^6$ M^{-1} s^{-1}).[14,15] Thus, if the reaction proceeds via a metal-based oxidant (reactions 6 and 7), the product profile will be unaffected by the use of MPPH since we have demonstrated that in genuine 2-electron alkene oxidations MPPH is a perfectly competent substitute for TBHP (in fact, the epoxidations of cyclohexene and *cis*-stilbene were more efficient with MPPH than with TBHP).[18] On the other hand, if the reaction proceeds via alkoxyl radical intermediates (reactions 8 and 9), the very fast β-cleavage of $PhCH_2CMe_2O^\bullet$ will lead predominantly to benzyl radical derived products. We have already applied the MPPH probe to a variety of hydroperoxide/iron/alkane systems finding only alkoxyl radical chemistry *in all cases*.[19] Consequently, it was no surprise to discover that there were essentially no cyclohexane oxidation products when MPPH was used in place of TBHP, the main products being benzaldehyde (average yield 5.8 mM, range 3.4–9.0 mM) together with some benzyl alcohol (average yield 1.1 mM, range 0–4.3 mM). These two compounds are presumably formed via reactions 10, 11, and 12.

$$PhCH_2^\bullet + O_2 \rightarrow PhCH_2OO^\bullet \qquad (11)$$

$$2PhCH_2OO^\bullet \rightarrow PhCHO + PhCH_2OH + O_2 \quad (12)$$
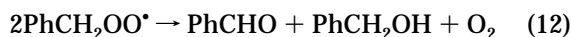
In dramatic contrast, the MPPH-induced oxidation of ethylbenzene and cyclohexene gave substantial quantities of the corresponding ketones and alcohols (Figure 1).[20] We attribute these products to autoxidation of these two hydrocarbons initiated by the benzylperoxyl radicals, viz.

$$PhCH_2OO^\bullet + {>}CH_2 \rightarrow PhCH_2OOH + {>}\dot{C}H \quad (13)$$

Further evidence that the chemistry in question is initiated by alkoxyl radicals (reactions 1 and 2) was obtained by the addition of two commercially important radical trapping antioxidants, 2,6-di-*tert*-butyl-4-methylphenol (BHT) and diphenylamine to otherwise "normal" systems containing 1.0 M ethylbenzene (EtPh), 20 mM TBHP, or 20 mM MPPH and 10 mM catalyst. Both of these antioxidants, AH, react rapidly with alkoxyl radicals ($k_{14}^{BHT} = 2.0 \times 10^7$ M^{-1} s^{-1},[13] $k_{14}^{Ph_2NH} = 3 \times 10^8$ M^{-1} s^{-1},[21]) *and* with alkylperoxyl radicals ($k_{15}^{BHT} =$
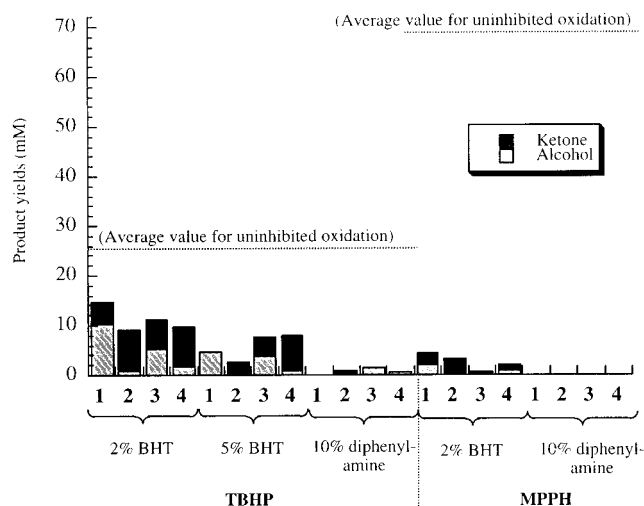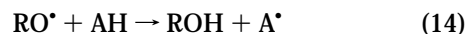
FIGURE 2. Effect of adding antioxidants to the oxidation of ethylbenzene by iron catalysts **1–4** and TBHP or MPPH at room temberature under an atmosphere of oxygen for 18 h.

1.4×10^4 M^{-1} s^{-1},[22] $k_{15}^{Ph_2NH} \approx 4 \times 10^4$ M^{-1} s^{-1}.[23]) Knowledge

$$RO^\bullet + AH \rightarrow ROH + A^\bullet \qquad (14)$$

$$ROO^\bullet + AH \rightarrow ROOH + A^\bullet \qquad (15)$$

of these antioxidative rate constants leads directly to three simple predictions. First, 100 mM Ph_2NH should completely inhibit the MPPH-promoted oxidations of EtPh by trapping all the benzylperoxyl radicals formed in reactions 10 and 11 before they can attack the hydrocarbon, reaction 13, i.e. $k_{15}^{Ph_2NH}[Ph_2NH]$ ($= 4 \times 10^4 \times 0.1 = 4 \times 10^3$ s^{-1}) $\gg k_{13}^{EtPh}$[EtPh] ($= 1.1 \times 1.0 = 1.1$ s^{-1}). This prediction was confirmed experimentally with all four catalysts (see Figure 2).[24] Although BHT is only one-third as active as Ph_2NH in trapping peroxyl radicals, even 20 mM BHT was sufficient to inhibit the MPPH-promoted oxidation of EtPh very strongly (Figure 2).[24] The second prediction is that 20 mM and 50 mM BHT should provide only partial inhibition of the *tert*-butoxyl radical initiated oxidation of EtPh since even 50 mM BHT can intercept only ca. 50% of the *tert*-butoxyl radicals formed in reaction 1, i.e. $k_{14}^{BHT}[BHT]$ ($= (2.0 \times 10^7) \times 0.05 = 1.0 \times 10^6$ s^{-1}) $\approx k_2^{EtPh}[EtPh]$ ($= (1.05 \times 10^6) \times 1.0 = 1.05 \times 10^6$ s^{-1}). The final prediction is that 100 mM diphenylamine should produce almost complete inhibition of EtPh oxidation promoted by TBHP, i.e. $k_{14}^{Ph_2NH}[Ph_2NH] = (3 \times 10^8) \times 0.1 = 3 \times 10^7$ s^{-1}. The validity of the second and third predictions are also attested to by the data shown in Figure 2.[24]

Our results provide unequivocal proof that Sawyer's "oxygenated Fenton chemistry" in organic solvents (and by implication in water) involves simple *free*-radical-mediated chemistry. It is not radical-free as Sawyer has suggested.[3,9] There are, of course, numerous enzymes, including cytochrome P450s and methane monooxygenases, which can effect alkane oxidations via high-valent iron–oxo species. However, mimicking these enzyme with simple chemical systems is not a trivial undertaking and, to our knowledge, has never been achieved with an iron catalyst and a tertiary alkyl hydroperoxide.[27] We conclude that mechanistic interpretation in this general area of biomimetic chemistry should only be drawn after exhaustive studies using a variety of experimental tests for the involvement of free radicals.[7,13,19,25–27]

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(2) NRCC Research Associate, 1995−1997.

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(4) Sawyer's nonradical mechanism involves initial formation of a peroxy−iron(II) species (formulated as [Fe^{II}OOR] ignoring the other ligands) which then reacts with O$_2$ to form another (quote) "*hypothetical*" intermediate, [Fe^{III}OOR(O$_2$)], which subsequently oxidizes alkanes to ketones. (Peroxy−iron(III) complexes are well established.[5] However, at least some of them have been demonstrated not to react *directly* with hydrocarbons.[5a,6])

(5) See, e.g.: (a) Barton, D. H. R.; Bévière, S. D.; Chavasiri, W.; Doller, D.; Liu, W.-G.; Reibenspies, J. H. *New. J. Chem.* **1992**, *16*, 1019−1029 and references cited. (b) Ménage, S.; Wilkinson, E. C.; Que, L., Jr.; Fontecave, M. *Angew Chem., Int. Ed. Engl.* **1995**, *34*, 203−205.

(6) Unpublished stop-flow experiments from this laboratory.

(7) See accompanying comment by Professor Cheves Walling.

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(10) (a) Oxidation of cyclohexane (1 M) by iron catalysts (10 mM) and alkyl hydroperoxides (20 mM) under an atmosphere of oxygen. Product yields (mM) are from duplicate experiments; results in brackets are from Table 3 in ref 9. (i) TBHP. Catalyst, ketone, alcohol, mixed peroxide: **1**, 2.7, 3.4 (4.8); 4.2, 4.7 (4.2); 0.2, trace, (0). **2**, 3.2, 3.9 (4.3); 1.3, 1.3 (6.1); 0, 0 (0). **3**, 2.9, 4.4 (3.7); 2.6, 3.4 (4.9); 0, 0 (0). **4**, 10.9, 10.7 (12); 0, 0 (0); trace, 0 (0). (ii) MPPH. Catalyst, ketone, alcohol, mixed peroxide, benzaldehyde, benzyl alcohol, bibenzyl, MPPOH: **1**, 0.5, 0.5; 0.9, 0.5; 0, 0; 3.8, 3.4; 4.3, 3.2; trace, trace; 0.5, 0.8. **2**, 0, 0; 0, 0; 0, 0; 4.5, 6.0; 0, 0; 0, 0; 3.3, 3.5. **3**, 0, 0; 0, 0; 0, 0; 5.7, 5.0; 0.4, 0; 0, 0; 0.3, trace. **4**, 0, 0; 0, 0; 0, 0; 9.0, 8.7; 0.3, 0.5; 0, 0; 0.6, 0.8. (b) Oxidation of cyclohexene (1 M) by iron catalysts (10 mM) and alkyl hydroperoxides (20 mM) under an atmosphere of oxygen. Product yields (mM) are from duplicate experiments; results in brackets are from Table 3 in ref 9. (i) TBHP. Catalyst, ketone, alcohol, epoxide, mixed peroxide: **1**, 14.4, 19.9 (71); 32.7, 45.5 (69); 0.3, 0.2 (0); 0.3, 0.4 (0.5). **2**, 34.1, 71.5 (60); 2.8, 6.5 (35); 0, 0 (0); 0.2, 0 (0.5). **3**, 112.5, 89.5 (86); 70.0, 59.2 (60); 6.0, 4.4 (0); trace, 0 (1.8). **4**, 49.5, 64.6 (45); 1.5, 2.1 (2.2); 0, 0 (0); 0, 0 (0.5). (ii) MPPH. Catalyst, ketone, alcohol, epoxide, mixed peroxide, benzaldehyde, benzyl alcohol, bibenzyl, MPPOH: **1**, 27.7, 27.0; 49.3, 75.0; 0, 0; 0, 0; 0.1, 0; 1.3, 1.5; 0.4, 0.2; 0, 0. **2**, 142.5, 168.0; 10.3, 10.7; 2.0, 2.1; 0, 0; 0, 0; trace, trace; 0, 0; 0, 0. **3**, 103.9, 65.9; 82.5, 59.6; 2.0, 0.6; 0, 0; 0, 0; 4.2, 2.7; trace, 0.3; 0, 0. **4**, 145.0, 158.5; 7.0, 7.5; trace, trace; 0, 0; 0, 0; 0, 0; 0, 0; 0, 0. (c) Oxidation of ethylbenzene (1 M) by iron catalysts (10 mM) and

alkyl hydroperoxides (20 mM) under an atmosphere of oxygen. Product yields (mM) from duplicate experiments, results in brackets are from Table 3 in ref 9. (i) TBHP. Catalyst, ketone, alcohol, mixed peroxide: **1**, 20.4, 18.7 (16); 10.7, 9.0 (9.2); 0, 0 (0). **2**, 18.5, 25.1 (38); 4.5, 0.6 (16); 0, 0 (0). **3**, 14.5, 13.1 (35); 11.1, 9.4 (11); 0, 0 (0). **3** + 10 mM benzaldehyde added prior to the addition of TBHP (7.0 mM and 5.3 mM benzaldehyde recovered in the duplicate experiments), 14.6, 13.0; 38.2, 36.5; 1.1, 1.0. **4**, 28.4, 26.3 (34); 3.4, 3.1 (0); 0, 0 (0). (ii) MPPH. catalyst, ketone, alcohol, mixed peroxide, benzaldehyde, benzyl alcohol, bibenzyl, MPPOH: **1**, 35.4, 52.8; 19.8, 23.2; 0, 0; 0.15, trace; 0.9, 1.0; 0, trace; 0, 0.6. **2**, 69.1, 46.1; 1.4, 9.5; 0, 0; trace, 0; 0, 0; 0, 0; 0, 0. **3**, 52.6, 40.2; 16.8, 22.4; 0, 0; 0, 0; 1.2, 1.5; 0, 0; 0.8, 1.0. **4**, 90.9, 78.8; 7.8, 4.5; 0, 0; 0, 0; 0, 0; 0, 0; 0, 0.

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(20) For ethylbenzene, PhCHO average yield = 0.02 mM, range 0−0.15 mM, PhCH$_2$OH average yield (after workup in the usual way[13,19] with Ph$_3$P to reduce hydroperoxides to alcohols) 0.6 mM, range 0−1.5 mM. For cyclohexene, the corresponding values are 0.01, 0−0.1, 1.5, and 0−4.2 mM. The small yields of benzaldehyde in these reactions are due to its oxidation as was demonstrated by the partial destruction of added benzaldehyde during the **3**/Me$_3$COOH-induced oxidation of ethylbenzene (see ref 10).

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(24) The effect of adding antioxidants (mole percent relative to substrate) to the oxidation of ethylbenzene (1 M) by iron catalysts (10 mM) under an

atmosphere of oxygen. Product yields (mM) from duplicate experiments: (a) TBHP (20 mM). Catalyst, no antioxidant, 2% BHT, 5% BHT, 10% Ph$_2$NH: Ketone: **1**, 20.4, 18.7; 3.4, 5.4; 0, 0; 0, 0. **2**, 18.5, 25.1; 7.2, 9.5; 2.3, 3.2; 0.4, 1.4. **3**, 14.5, 13.1; 5.8, 6.2; 5.9, 2.4; 0, 0. **4**, 28.4, 26.3; 8.0, 7.8; 7.7, 6.4; 0, 0. Alcohol: **1**, 10.7, 9.0; 10.4, 10.3; 4.8, 4.7; 0, 0. **2**, 4.5, 0.6; 1.2, 0.3; 0, 0; 0, 0. **3**, 11.1, 9.4; 6.2, 4.4; 4.9, 2.7; 1.1, 1.9. **4**, 3.4, 3.1; 2.6, 1.0; 1.2, 0.8; 0.5, 0.1. (b) MPPH (20 mM) + 2% BHT. Catalyst, ketone, alcohol, mixed peroxide, benzaldehyde, benzyl alcohol, bibenzyl, MPPOH. **1**, 2.6, 2.0; 2.7, 1.6; 0, 0; 2.2, 1.3; 1.8, 1.4; 0, 0; 2.8, 3.0. **2**, 0.7, 5.8; 0, 0.2; 0, 0; 0.8, 1.7; 0, 0.1; 0, 0.4; 0.8, 2.0. **3**, 1.4, trace; 0, 0; 0, 0; 1.6, 2.1; 0, 0; trace, 0; 4.1, 7.3. **4**, 0.9, 1.2; 0, 2.0; 0, 0; 3.2, 2.8; 0, 0; 0, 0; 2.0, 2.0. (c) MPPH (20 mM) + 10% Ph$_2$NH. Catalyst, ketone, alcohol, mixed peroxide, benzaldehyde, benzyl alcohol, bibenzyl, MPPOH: **1**, 0, 0; 0, 0; 0, 0; 2.7, 2.7; 6.3, 6.4; trace, 0; 0.2, 0.2. **2**, 0, 0; 0, 0; 0, 0; 12.1, 12.3; 0.4, 0; 0, 0; 0, 0. **3**, 0, 0; 0, 0; 0, 0; 5.7, 6.0;

4.2, 4.3; 0, 0; 0.3, 0.2. **4**, 0, 0; 0, 0; 0, 0; 11.5, 11.2; 0, 0; 0, 0; 0, 0.

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