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High-Pressure Competitive Hydrogenation of Aldehydes, Ketones, and Olefins on Copper Chromite Catalyst

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Relative reactivities of 4 saturated acyclic aldehydes, 15 saturated acyclic and cyclic ketones, and 11 acyclic and cyclic olefins were determined in the copper chromite-catalyzed vapor-phase hydrogenation of binary and ternary mixtures, at 150–250°C, under 20–100 bars total pressure, with excess hydrogen, in a continuous-flow reactor. A specific feature of the copper catalyst is the higher reactivity of C=O bonds, when compared to C=C bonds: C=O (aldehyde) > C=O (ketone) > C=C (olefin). Alkyl substituents at the double bond lower the reactivities and cause some overlap between the three groups. The following scale of reactivity R, with methyl isobutyl ketone as reference compound ($R = 1$), was found at 185°C and 80 bars: aldehydes, $R = 3$–5; cyclic ketones, $R = 1$–2; acyclic ketones and n-olefins, $R = 0.6$–1.6; cyclic olefins, $R = 0.3$–0.6; trisubstituted olefins, $R = 0.03$–0.2. Phenyl substituents strongly activate both the C=C and C=O bond hydrogenation; the phenyl ring is not hydrogenated. Changes of R values with temperature and pressure do not modify the reactivity sequence; at higher pressures, all R values become closer to 1. An attempt was made to extend the above scale of reactivity to double bonds included in the same molecule, in the hydrogenation of eight olefinic aldehydes and ketones. A good prediction of selectivity is possible for nonconjugated compounds; unsaturated alcohol formation is therefore frequently favored in copper chromite catalysis. However, the prediction breaks down in conjugated compounds; the C=C—C=O group apparently reacts as a single entity, and the C=C reactivity is enhanced.

INTRODUCTION

Results of competitive hydrogenation for 19 ketones have been reported in the previous work of this series (*1*). High-pressure continuous-flow experiments (120–250°C and 20–100 bars) are run in stainless-steel equipment (*2*) under steady-state conditions in the vapor phase, and occasionally in the liquid phase. The copper chromite catalyst (Harshaw, ref. Cu-0402T) in ⅛-in. pellets was prereduced in the reactor; its active phase is highly divided copper metal.

In the present work, binary and ternary mixtures of aldehydes, ketones, and olefins were hydrogenated under similar conditions in order to measure the relative reactivities of these compounds, and extend the scale of reactivity previously established for ketones at 185°C.

Knowledge of relative reactivities of C=O and C=C bonds should allow the prediction of selectivity in the hydrogenation of olefinic aldehydes or ketones (enal or enone) to the saturated aldehyde or ketone (al or one) or the unsaturated alcohol (enol). This point will be verified on a number of examples, with conjugated and nonconjugated double bonds.

EXPERIMENTAL

Catalyst, reactor and analytical (chromatographic) procedures will be found elsewhere (*1, 2*).

Commercial reagents, pure grade, were distilled before use under nitrogen atmosphere. Vapor-phase hydrogenation of high-boiling compounds requires sufficiently high temperatures and hydrogen/

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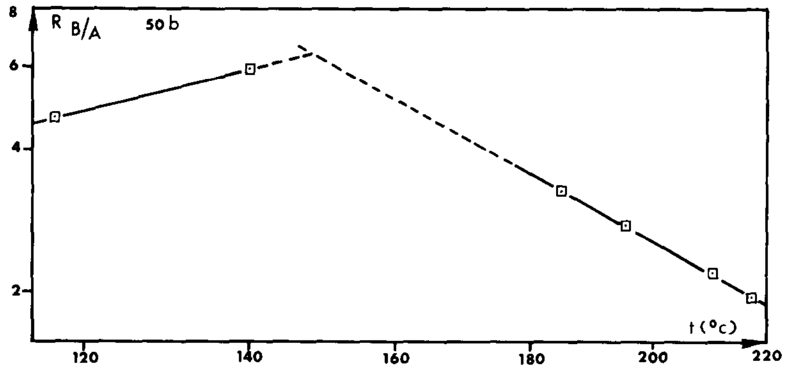


FIG. 1. Temperature effect on the relative reactivity in hydrogenation of a mixture: 5-methyl-2 hexanone (A)–*n*-heptanal (B), at constant pressure: vapor phase, 50 bars, *r*: 30–50; liquid phase, 50 bars, *r*: 12–30. Abscissae: Arrhenius 1/*T* K scale from right to left, *T*°C indicated; ordinates: log of reactivity $R_{B/A}$, values of $R_{B/A}$ indicated.

reagent ratios (*r*) to avoid condensation; hence the importance of the boiling point.

The saturated aldehydes R–CHO comprised linear (R = n-C_4H_9, n-C_5H_{11}) and branched (2-Et-butanal and hexanal) species; saturated ketones are those mentioned in the previous paper (*1*) (C_3 to C_9) plus the 1-phenyl-propanone. Olefins included normal (1-C_6H_{12}, 1-C_8H_{16}, 1-$C_{10}H_{20}$, 7-$C_{14}H_{28}$), branched (2-Me-1-butene, 2-Me- and 2,4,4-Me_3-2-pentene), and cyclic terms (cyclohexene and -octene, α-pinene, indene) compounds. Boiling points are between 40 and 250°C.

The unsaturated aldehydes and ketones comprised mono- (Δ^3-cyclohexene-1-carbaldehyde, 3,7-dimethyl-6-octanal, 3-phenyl-2-propanal, 5-hexen-2-one, 4-methyl-3-penten-2-one, 6-methyl-5-hepten-2-one, 3,3,5-trimethyl-2-cyclohexen-1-one) and di-olefinic (3,7-dimethyl-2,6-octadienal) compounds. Boiling points are between 120 and 250°C; for these last compounds, the trivial names are commonly used as short writing.

RESULTS

a. Aldehyde–Ketone Competitive Hydrogenations

Preliminary experiments indicate that side reactions (aldolization, hemiacetalization), not observed with ketones, lead to small amounts of C_{2n} products from the C_n aldehyde, but do not interfere at low conversion levels.

Temperature and pressure effects on the relative reactivity ratio *R* defined in (*1*) are illustrated in Figs. 1 and 2. The break in the curve (Fig. 1) indicates the discontinuity caused by the formation of a liquid phase at low temperatures.

The results of a large number of experiments are condensed in Fig. 2, where the index *I* is to 4-methyl-2-pentanone; the high reactivity of aldehydes, when compared to that of ketones, is obvious ($I > 1$).

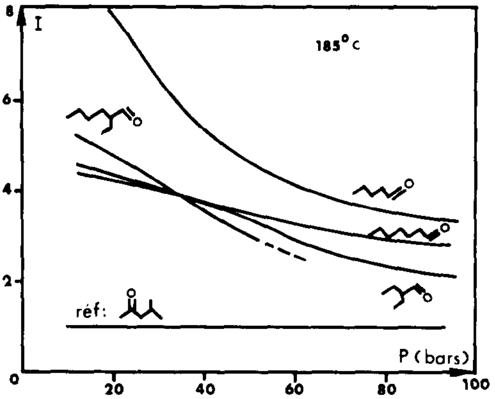


FIG. 2. Pressure effect on the relative reactivities in hydrogenation of the aldehydes with reference to 4-methyl-2-pentanone, at 185°C. For the scale, see legend to Fig. 2.

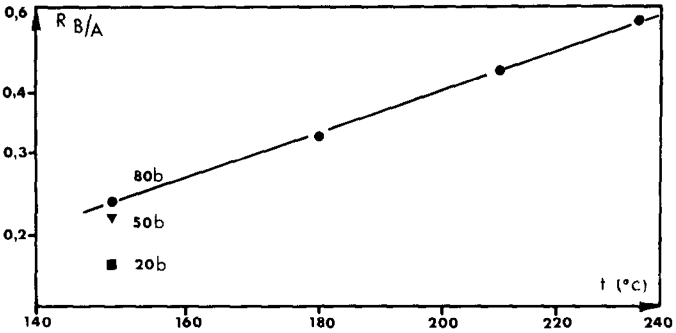


FIG. 3. Temperature effect on the relative reactivity in hydrogenation of a mixture: 2-pentanone (A)–cyclohexene (B) at constant pressure of 80 bars. For the scale, see legend to Fig. 1.

b. Olefin–Ketone (or Aldehyde) Competition

A preliminary study has indicated a great similarity of kinetic orders for cyclohexene and cyclohexanone (*2*) hydrogenations on copper chromite; the technique of competitive hydrogenation may therefore be applied to mixtures of olefins and carbonyl compounds. A detailed investigation of the pair 2-pentanone (A)–cyclohexene (B) at 180°C and 80 bars gives a constant value of $R_{B/A} = 0.33$. Changes with pressure and temperature are shown in Fig. 3 (activation energy = 4.5 kcal/mole under 80 bars pressure).

A number of other binary and ternary mixtures was investigated and numerical values of R are reported in Table 1. Direct competition between aldehydes and olefins lead to large errors in R values, due to the large differences of reactivities, except in particular cases. Thus, with the pair 2-ethylhexanal (A)–1-decene (B), $R_{B/A}$ approaches 1 at high pressure and temperature. As a rule, however, olefins are much less reactive than ketones and aldehydes.

Consistency of the R values is checked in two ways:

1. $R_{B/A}$ must be the same in binary (A + B) and ternary mixtures (A + B + C) (Fig. 4).

2. The transitivity relationship $R_{C/A} = R_{C/B} \times R_{B/A}$ must hold and may be used to calculate unknown reactivities (Fig. 5).

Side reactions were observed at higher temperatures (220°C) with aldehydes (traces of CO in the outgoing H_2 stream) and with indene (9% hydrogenolysis to 1-methyl-2-ethyl-benzene) (*5*). The benzene ring is practically untouched in benzene, toluene (180°C and 50 bars), and indene (220°C and 50 bars) reactions, a well-known property of copper catalysts (*4*).

c. General Scale of Reactivity

The results of experiments reported in Sections b and c, above, and in the previous paper (*1*), are now presented on a general scale of reactivity for C=C and

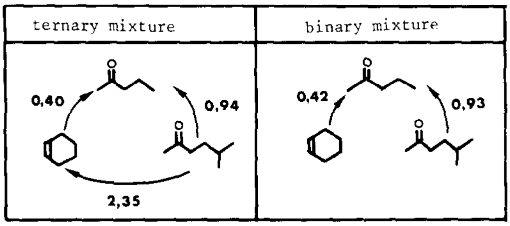


FIG. 4. Equality of relative reactivities in binary and ternary mixtures. Values of $R_{B/A}$ are indicated on the arrow B → A: vapor phase, 202°C and 80 bars.

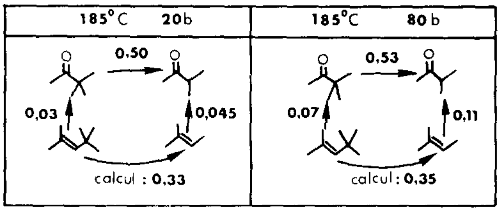


FIG. 5. Calculation of relative reactivities by the "transitivity relationship." See legend to Fig. 5.

TABLE 1

Relative Reactivity Ratios R in Hydrogenation of Binary and Ternary Mixtures on Copper Chromite Catalyst

Mixtures	Hydrogenation conditions (°C/bars)			
(A) 4-Methyl-2-pentanone	185/20	185/50	185/80	185/90
(B) Cyclohexene	$R_{B/A} = 0.33$	0.43	0.45	0.47
(A) 3,3-Dimethyl-2-butanone	185/20	185/50	185/90	
(B) 2,4,4-Trimethyl-2-pentene	$R_{B/A} = 0.03$	0.04	0.06	
(A) 3-Methyl-2-butanone	185/20	185/80		
(B) 2-Methyl-2-butene	$R_{B/A} = 0.045$	0.11		
(A) 2-Pentanone	185/20	185/50	185/90	
(B) α-Pinene	$R_{B/A} = 0.08$	0.20	0.24	
(A) 2-Heptanone	260/50			
(B) 7-Tetradecene	$R_{B/A} = 1.2$			
(A) Cyclohexene	185/80			
(B) Cyclooctene	$R_{B/A} = 1.04$			
(A) 1-Hexene	185/20	185/50	185/75	185/95
(B) 1-Octene	$R_{B/A} = 1.15$	1.20	1.22	1.22
(A) Cyclohexanone	218/20	218/50		
(B) Indene	$R_{B/A} = 1.35$	1.55		
(A) 2-Pentanone	202/80			
(B) Cyclohexene	$R_{B/A} = 0.4$	$R_{C/A} = 0.94$ $R_{C/B} = 2.35$		
(C) 5-Methyl-2-hexanone				
(A) 3-Pentanone	185/50	215/50		
(B) 1-Octene	$R_{B/A} = 0.74$	0.78		
(C) Cyclooctene	$R_{C/A} = 0.42$	0.60		
(A) 2-Ethylhexanal	215/20	215/50	215/80	
(B) 1-Decene	$R_{B/A} = 0.45$	0.6	0.8	

C=O bond hydrogenation on copper chromite catalyst, taking 4-methyl-2-pentanone as a reference compound A. The index of reactivity I for any compound X is defined as

$$I = R_{X/A}.$$

Values of I at 185°C are plotted on a log scale (I = 0.01 to 10) vs pressure in the curves of Fig. 6. Some of the compounds investigated have been omitted for the sake of clarity (see Fig. 2, this paper, and Fig. 3, Ref. (1)). The following sequence of decreasing reactivity emerges from this diagram (at 80 bars):

Compound	I
aldehydes	3 -5
cyclic ketones	1 -2
acyclic ketones and linear olefins	0.6 -1.6
cyclic olefins	0.3 -0.6
trisubstituted olefins	0.03-0.2

which may be summarized as:

$$\mathrm{C{=}O\ (aldehyde)} > \mathrm{C{=}O\ (ketone)} > \mathrm{C{=}C}.$$

However, within each family, alkyl substitution at the double bond lowers the reactivity, causing some overlap between the groups.

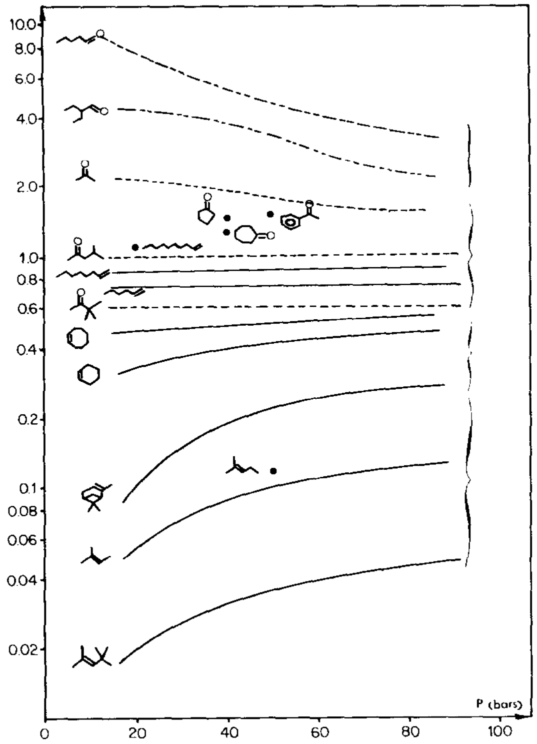


FIG. 6. Relative reactivities of aldehydes, ketones, and olefins with reference to 4-methyl-2-pentanone in vapor-phase hydrogenation at 185°C, as a function of pressure.

These effects of substitution have been assigned to steric hindrance in the case of ketones (*1*); considering the sequence of reactivity at 80 bars (Fig. 2), *n*-butanal > *n*-heptanal > 2-ethylbutanal > 2-ethylhexanal, this conclusion may be extended to the aldehydes (hydrogenoalkyl ketones). Sporka and Ruzicka (*13*) correlated hydrogenation rates of aldehydes on a Cu-kieselguhr Catalyst at 190°C/1 atm (R–CHO, R = C_2H_5, n-C_3H_7, i-C_3H_7, C_4H_9, i-C_4H_9, n-C_5H_{11}, n-C_6H_{13}, n-C_7H_{15}) with the Taft σ coefficients, indicating the predominance of inductive effects. However, no competitive hydrogenation results were reported by these authors, and working pressures are very different from ours.

The reactivity of acyclic olefins obey Lebedev's rule (*3*),

$$-CH{=}CH_2 > -CH{=}CH- > \; >C{=}CH-,$$

and are also explained by steric hindrance effects of substituents. The increase of reactivity with chain length of normal α-olefins is, however, unexplained; these olefins are more reactive than the most hindered ketones. No cycle effect is noticed for cyclic olefins which occupy the rank expected for acyclic bisubstituted olefins; the same unexplained chain-length effect is observed (cyclo-octene > cyclohexene).

Values of I at 220°C are plotted vs pressure in the curves of Fig. 7; this diagram includes high-boiling compounds not indicated in Fig. 6. The high reactivity of indene and 1-phenyl-propanone, when compared to similarly substituted olefins or ketones, points to the strong activating effect of the phenyl substituent on C=C and C=O bonds. The benzene ring is not hydrogenated (*4*): I = 0.002 for benzene 220°C and 50 bars.

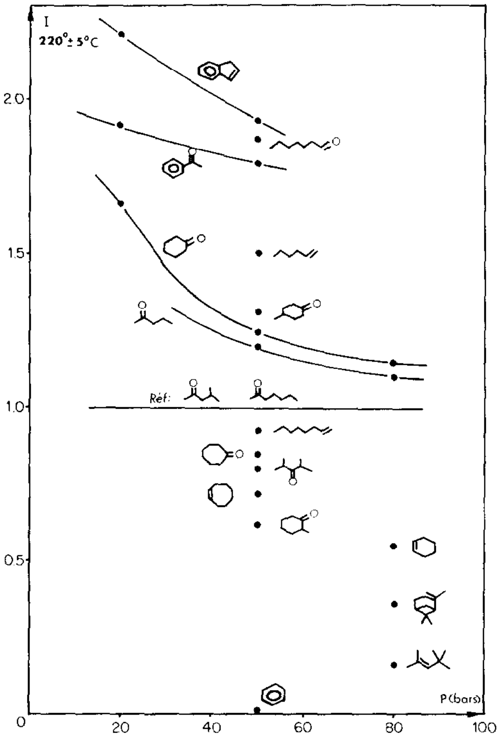
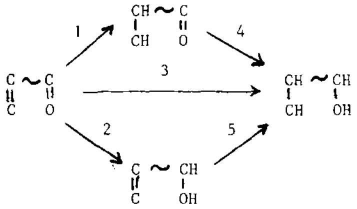


FIG. 7. Relative reactivities of aldehydes, ketones, and olefins with reference to 4-methyl-2 pentanone, in vapor phase hydrogenation at 220°C, as a function of pressure.

These two facts may be related; the phenyl group has been reported as activating on Pd catalysts, and deactivating on Pt catalysts, during the hydrogenation of arylolefins (*6*). Pd, like Cu, is a much less active catalyst than Pt in benzene hydrogenation (*7*). A generalization would be that phenyl activation implies a weak adsorption of the aromatic ring on active centers (Cu, Pd).

d. Hydrogenation of Unsaturated Aldehydes and Ketones

The hydrogenation of olefinic aldehydes (enal) or ketones (enone) is described by a formal "square" kinetic scheme:



The products are the saturated aldehyde (al) or ketone (one), the olefinic alcohol (enol), and the saturated alcohol (ol). Isomerization of enol to ketone is not observed on Cu catalysts. A selective conversion to the saturated aldehyde or ketone is readily obtained with a number of metal catalysts such as Pd, Pt, and Ni; only traces of enol are found (*6b*, *8*, *9*), and the conversion to enol of unsaturated aldehydes or ketones is a difficult problem of organic catalysis. If the reactivity scale established above (Section c) remains valid when both C=C and C=O double bonds belong to the same molecule, copper chromite should be a good catalyst for selective enol formation. In effect, at low conversion levels, if reaction 3 is not too fast, the ratio of reaction rates r_2/r_1 (and therefore of selectivities S_2/S_1 for enol and one or al) should be equal to the reactivity ratio $R_{CO/CC}$, frequently high on copper chromite. This prediction was put to the test with eight unsaturated aldehydes and ketones, with

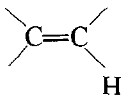
TABLE 2

Hydrogenation of Nonconjugated Unsaturated Aldehydes and Ketones

Compounds and conditions (°C/bars)	Conversion (%)	Selectivities (%)		
		enol	one	ol
(a) 6-Methyl-5-hepten-2-one	10	85	0.5	14.5
210/50 *r*: 20–30 vapor phase	53	71	1.5	27.5
140/50 *r*: 12 liquid phase	13	99	—	—
(b) 3,7-Dimethyl-6-octen-1-al				
235/50 *r*: 35 vapor phase	90.5	35.8	43.5	20.7
180/50 liquid phase	88.5	48.2	46.8	5
(c) Δ3-Cyclohexene-1-carbaldehyde				
210/50 *r*: 40 vapor phase	61	65	1	34
135/50 *r*: 40 liquid phase	16	91	8.5	0.5
(d) 5-Hexen-2-one				
185/50 *r*: 18 vapor phase	45	6.5	17.5	77
110/50 *r*: 10 liquid phase	26	11.5	79	9.5

conjugated and nonconjugated C=C and C=O bonds.

1. Nonconjugated double bonds (*see Table 2*). In the three cases (a), (b), (c) a high selectivity to enol is expected in view of the *I* indices (see the previous section):

(a) R—CO—CH$_3$	$I \simeq 1$		$I \simeq 0.03\text{–}0.2$
(b) >C—CHO	$I \simeq 2$	—∂°—	$I \simeq 0.03\text{–}0.2$
(c) ∂°	$I \simeq 3$	cyclohexene	$I \simeq 0.04$

and observed in cases (a) and (c) (this last reaction has been reported before (*6*, *10*)). A low selectivity is expected and observed for case (d):

(d) R—CO—CH$_3$	$I \simeq 1$	—CH=CH—	$I \simeq 1$.

A competitive experiment at 185°C and 50 bars with the pair 2-hexanone (A)–1-hexene (B) gives $R_{B/A} = 0.66$.

In conclusion, copper chromite has, in favorable cases, an excellent selectivity for enol formation if compared with other metal catalysts.

2. Conjugated double bonds (*see Table 3*). The *I* indices predict a high enol selectivity in case (a) (mesityl oxide) and a competitive hydrogenation of the structurally related 4-methyl-2-pentanone (A)–2-methyl-2-pentene (B) pair has given $R_{B/A} = 1/25$ at 164°C and 50 bars; in fact, the enol yield is very low.

Cases (b) and (c) are similar, though less favorable. These low yields of enol imply an unexpectedly high C=C reactivity in conjugated C=C—C=O systems.

3. 3,7-Dimethyl-2,6 octadien-al (*citral*).

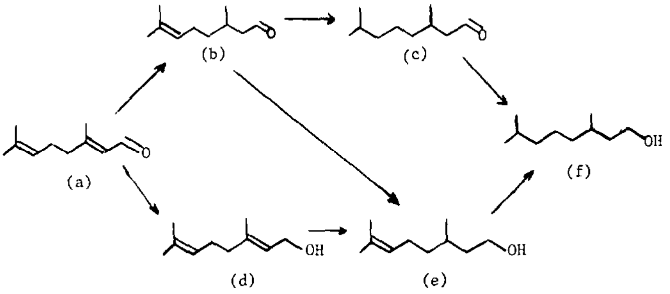
TABLE 3

Hydrogenation of Conjugated Unsaturated Aldehydes and Ketones

Compound and conditions (°C/bars)	Conversion (%)	Selectivities (%)		
		enol	one	ol
(a) 4-Methyl-3-penten-2-one				
164/50 r: 16 vapor phase	10	6	78	16
190/50 r: 27 vapor phase	20	8	68	24
(b) 3,3,5-Trimethyl-2-cyclohexene-1-one				
235/50 r: 27 vapor phase	35	0	15	85
182/50 r: 18 liquid phase	24	1.8	57.3	40.9
(c) 3-Phenyl-2-propen-1-al				
275/50 r: 30 vapor phase	86	4	40	56
184/50 r: 17 liquid phase	15.7	14	63	23

In this interesting case, two identical C═C bonds (trisubstituted) and a C═O aldehyde bond are present. The reactant (a) is a mixture of *cis* (neral) and *trans* (geranial) stereoisomers, with a *cis/trans* ratio of 55/45. The general scale of reactivities predicts a high yield of dienol; the following hydrogenation tests do not support this prediction:

	Conversion (%)	Selectivities (%)				
		enal (b)	al (c)	dienol (d)	enol (e)	of (f)
Vaporphase (°C/bars) 260/50 r:40	50.2	4.5	6.5	10.5	61.5	15
Liquid phase (°C/bars) 180/50 r:20	36.3	4.5	19	17	52	7.5



Of the two identically substituted C═C bonds, the one conjugated to C═O reacts faster: only 10% of the products retain this structure at 50% conversion in the vapor phase (17% in the liquid phase at 36% conversion), while the other double bond in position 6 remains present in 76% of the vapor-phase products (73% in the liquid phase). The C═O aldehyde bond is retained in 11% of the products of vapor-phase hydrogenation (23% in liquid phase). Therefore, the conjugated structure C═C—C═O apparently reacts as a single entity to give comparable amounts of CH—CH—C═O and C═C—CH—OH, at a much faster rate than the isolated C═C bond: the primary products are the enal (b) and the dienol (d). Further hydrogenation of the enal (b) nonconjugated gives the al (c) and enol (e) in proportion to the scale of reactivities, as shown above, that is, mostly (e) (competition between the trisubstituted C═C and the aldehyde C═O). Further hydrogenation of the dienol (d) should produce a mixture of isomeric enols with the double bond in the 6 (e) or 2 (e′) position: the absence of (e′) indicates that the double bond in the 2 position is activated by the alcohol function (allylic system).

In conclusion, the reactivity of a conjugated C═C bond in the C═C—C═O structure is strongly enhanced and becomes comparable to the C═O reactivity. The general scale of reactivity indices cannot be applied to this bond, and enol formation is much less selective than expected.

DISCUSSION

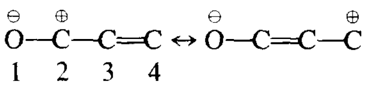
The relative reactivity of C═O and C═C bonds in competitive hydrogenation reflects the competition of adsorption of these groups on active centers (1).

The higher reactivity of the C=O bond vs a similarly substituted C=C bond (e.g., *n*-heptanal vs 1-octene) is a specific property of the copper catalysts. The reverse is true with platinum metal catalysts (*11*). Chemisorptive differences between Cu and group VIII metals are well documented (*12*); the low heats of adsorption of simple gases on copper (<10 kcal/mole) suggest dipole interactions rather than covalent bond formation. In such a case, the higher polarization of the C=O bond ($C^{+}\text{-}O^{-}$) could explain the higher chemisorption rates of carbonyl groups.

Steric effects of substituents hindering the approach of the functional group toward active centers on the surface are expected, and well known for olefins (Lebedev's rule (*3*)). Our results show that these effects are usually stronger in liquid-phase hydrogenation.

A phenyl substituent increases the reactivity of both C=O and C=C groups (e.g., indene, acetophenone); classical resonance effects favoring the double-bond polarization may account for this observation. The adsorption and hydrogenation of the benzene ring suppresses this effect on other catalysts such as Pt (*7*).

The scale of reactivity obtained in competitive hydrogenation of monofunctional compounds may be extended to nonconjugated bifunctional molecules (olefinic aldehydes and ketones). A high selectivity of enol formation was observed, as predicted, when an unhindered C=O was associated with a hindered C=C. However, the prediction breaks down with conjugated C=C—C=O systems: both double bonds react at similar rates, and enol selectivity is lower than expected. This suggests a nucleophilic attack of the conjugated system



$$\overset{\ominus}{\underset{1}{O}}-\overset{\oplus}{\underset{2}{C}}-\underset{3}{C}=\underset{4}{C} \leftrightarrow \overset{\ominus}{O}-C=C-\overset{\oplus}{C}$$

leading respectively to C=C—CH—OH and CH—C=C—OH ⇄ CH—CH—C=O (1-2 and 1-4 additions) as in metal hydride reductions. Copper chromite catalyzed hydrogenation, and copper hydride reduction (*14*) of enones present in this respect a striking similarity: both favor 1-4 addition of hydrogen.

In conclusion, the scale of reactivity reflects catalyst specificity and structural properties of the hydrogenated molecule; selectivity cannot be assigned to the catalyst only.

ACKNOWLEDGMENT

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